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XX.—CAMPHORIC ACID.

[ELEVENTH PAPER.]

CONFIRMATION OF BREDT'S FORMULA; SOME DERIVATIVES OF INACTIVE CAMPHORIC ACID.

BY WILLIAM A. NOYES AND AUSTIN M. PATTERSON.

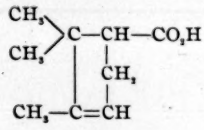
Some time ago one of us[1] prepared synthetically the 2.3,3-trimethylcyclopentanone and proved it to be identical with a ketone prepared from dihydro-β-campholytic acid. This was the first synthesis of a cyclic derivative of camphor, and confirmed the view previously expressed by Blanc as to the structure of β-campholytic acid. In the same connection, the opinion was expressed[2] that the relation between α-campholytic acid ("cistranscampholytic acid") and β-campholytic acid ("ciscampholytic acid") is one of stereoisomerism. Later, further evidence pointing in the same direction has been furnished.[3] Results obtained, however, by Kershbaum

[1] This JOURNAL, **23**, 130.

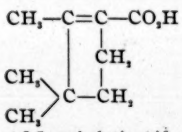
[2] *Loc. cit.*, p. 134.

[3] Noyes and Phillips: This JOURNAL, **24**, 285; Noyes and Blanchard: *Ibid.*, **26**, 283.

and Tigges,[1] by Blanc,[2] and by Lapworth[3] are quite inconsistent with this conclusion and point to the following relation between the two acids:



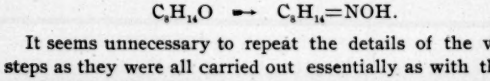
α-Campholytic acid.



β-Campholytic acid.

According to these formulas, the transformation of the α- to the β-acid is accompanied by a transfer of a methyl group from the α- to the β-position, as well as by a shifting of the double union. A new, and apparently a very decisive, proof that such a transfer occurs has now been obtained.

In the last paper[4] the preparation of dihydro-α-campholytic acid was described. This acid has now been carried through the same series of transformations which were some time ago applied to the dihydro-β-campholytic acid[5] ("dihydrociscampholytic acid" or "dihydroisolauronolic acid"). These transformations are:



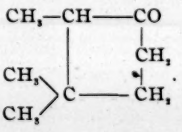
It seems unnecessary to repeat the details of the various steps as they were all carried out essentially as with the isomeric acid. The shaking of the ester of the α-bromdihydrocampholytic acid with an aqueous solution of barium hydroxide was continued for ten days at a temperature of 40° to 50°, and the decomposition was then still far from complete. The saponification and decomposition were finally completed by boiling the mixture with an upright condenser for some

[1] Ber. d. chem. Ges., **33**, 2938.
[2] Compt. rend., **131**, 803.
[3] J. Chem. Soc. (London), **79**, 1284.
[4] This JOURNAL, **26**, 288.
[5] *Ibid.*, **22**, 262.

hours. The mixture of the hydroxy acid and the Δ^5-campholytic acid[1] obtained, was separated by neutralizing with ammonia and distilling with steam. The ammonium salt of the Δ^5-acid dissociates readily and passes over, while the larger portion of the hydroxy acid remains behind. The latter was obtained only as an oil. It forms a difficultly soluble calcium salt which was analyzed. The salt dried at 110° gave 10.53 per cent of calcium. Theory requires 10.46 per cent. The amount of the hydroxy acid obtained was very much smaller than in working with the isomeric acid, and only a few centigrams of the oxime of the ketone were finally secured. It was possible to crystallize the oxime from ligroin, however, and to secure what seemed to be a quite perfect purification.

The new oxime, which must be that of 2,2.3-trimethylcyclopentanone, crystallizes in plates which melt at 104°, curiously enough, at exactly the same temperature as does the oxime of the 2.3,3-trimethylcyclopentanone mentioned above. The latter, however, crystallizes in needles instead of plates, and a mixture of the two melts at 80° or below. There can, therefore, be no doubt that the two oximes, and hence the two ketones, are different.

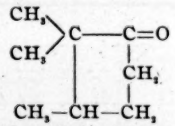
If the two campholytic acids were stereomeric compounds, as one of us formerly supposed, the ketones prepared from the two dihydro acids would each have the structure



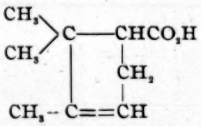
A ketone of this structure can exist in two optically active and in an inactive form, but there can be no "cis" and "trans" isomerism. Since the campholytic acids used in each case were inactive, the resulting ketones and oximes must also be inactive, and the fact that they are different establishes for them a different structure. The only rational explanation of such a result seems to be that of the wandering of a methyl

[1] This JOURNAL, **26**, 291.

group in the transformation of either campholytic acid into the other. This leads to the following formulas for the new ketone and for α-campholytic acid:



2,2,3-Trimethylcyclopentanone.

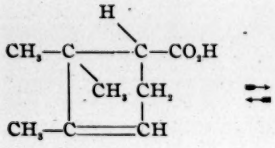


α-Campholytic acid.

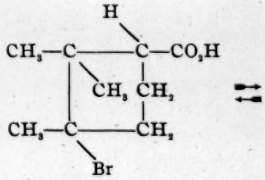
This result furnishes, as has been stated, a new and very positive confirmation of Bredt's formula.

Before leaving this part of the subject it seems worth while to point out that the work done with the campholytic acids has brought out certain facts which cannot be readily explained by the current stereochemical theories and which seem, in part, at variance with those theories.

First, the addition of hydrobromic acid to α-campholytic acid should give rise to two configurations according as the acid adds itself on the one side or the other of the plane of the ring. In one of these the bromine and carboxyl would be "cis," in the other "trans." But it has been shown in a previous paper[1] that a single configuration is almost or quite exclusively formed. This must be the "cis" form, if camphoric acid has the "cis" configuration, as is usually supposed. Second, the transformations of α-campholytic acid to β-campholytic acid, and *vice versa*, are supposed to occur through the following steps:

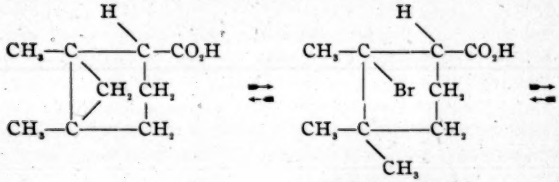


α-Campholytic acid.

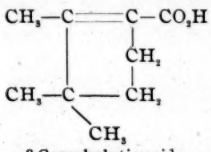


Hydrobromide of α-campholytic acid.

[1] This JOURNAL, 24, 291.



Hydrobromide of β-campholytic acid.



β-Campholytic acid.

An examination of these formulas shows that the bromine and carboxyl of the hydrobromide of β-campholytic acid are *cis* when it is derived in this manner from α-campholytic acid, while they should be *trans* if derived directly from the β-campholytic acid. Assuming camphor and camphoric acid to have the *cis* configuration, no consistent explanation of the facts along such lines seems possible.

While the stereochemical theories have been very successful in explaining optical isomerism and in predicting the number of possible isomers, they occasionally break down completely when the attempt is made to apply them logically to questions of the above description.

The work here described was already practically complete when an article by Blanc[1] appeared in which he describes the preparation of a ketone through the following series of compounds :

$$\underset{\alpha\text{-Campholenic acid.}}{C_8H_{13}CH_2CO_2H} \rightarrowtail C_8H_{15}CH_2CO_2H \rightarrowtail C_8H_{15}CHBrCO_2H \rightarrowtail$$

$$C_8H_{14}{=}CHCO_2H \rightarrowtail C_8H_{14}O.$$

[1] Bull. Soc. Chim., **27**, 71.

The oxime of this ketone melts at 107° to 108° and is different from the oxime of the ketone from dihydro-β-campholytic acid, and on this fact Blanc bases the conclusion that it must have a different structure. But the α-campholenic acid is optically active, and if that activity continues through the series the ketone obtained by Blanc might be, so far as the evidence goes, simply one of the active components of the racemic ketone obtained from dihydro-β-campholytic acid. The proof is, therefore, inconclusive, while the evidence given here is based on work with racemic compounds throughout, and leads to a conclusion which seems to be very positive. Except on the supposition that Blanc's ketone was in reality active, it seems difficult to reconcile the fact that his oxime melts at a temperature 3° to 4° higher than ours.[1]

In previous papers the opinion has been expressed that α-campholytic acid has a structure in which there is no asymmetric carbon atom and a stereomeric structure which would account for its optical activity was proposed.[2] This formula is, of course, no longer tenable.

Derivatives of Inactive Camphor.

A short time ago the attention of one of us was called to the fact that the Ampère Electro-Chemical Company, of New York, has been preparing to manufacture artificial camphor. The details of the process are not yet public, but the starting-point is, of course, turpentine. Through the kindness of the company we have been furnished with about 400 grams of their product. It is genuine *inactive* camphor. It melts at 176° and is optically inactive. On oxidation with nitric acid[3] it conducts itself in the same manner as ordinary camphor and yields *i*-camphoric acid melting at 204°, and this by

[1] Since writing the above we have received a sample of this oxime, which Dr. Blanc has very kindly sent us. We find that it melts about 3° higher than our oxime, but that a mixture of the two melts partially at the melting-point of our oxime, 103° to 104°. We are not aware that any one has recorded observations as to the melting-point of the mixture of a racemic compound with one of its active components, but it would seem that these observations agree best with the supposition that Dr. Blanc's oxime is active while ours is racemic. It is also possible that ours is not quite pure. Dr. Blanc writes us that he will repeat the preparation of his ketone, starting with inactive camphor.

[2] This JOURNAL, **24**, 287.

[3] *Ibid.*, **16**, 501.

treatment with acetic anhydride and acetyl chloride[1] gave camphoric anhydride melting at 225°. The nitric acid mother-liquors, after the oxidation, gave, on evaporation to dryness, solution of the residue in ammonia, adding barium chloride and warming, a copious crystalline precipitate, evidently barium camphoronate.[2]

In the last paper[3] an account of an inactive dihydrohydroxycampholytic acid and of its separation into the active components was given. On that work, chiefly, was based the view that the racemic α-campholytic acid used as the starting-point for the present study differs from the ordinary α-campholytic acid only in its optical inactivity. Since experience has shown that molecular rearrangements are especially frequent with this class of compounds, it is important to check every point as far as possible by independent observations which may lead to the same conclusion. In the present case it was, therefore, interesting to prepare the *i*-dihydrohydroxycampholytic acid directly from the *i*-camphor. This has been done.

Fifty grams of the *i*-camphoric anhydride were suspended in 100 cc. of alcohol, ammonia gas was passed in till solution was complete and the resulting solution was distilled slowly, while a slow current of ammonia was continued till the boiling-point of the imide was reached. The resulting imide[4] was not purified but was dissolved in 140 cc. of a 15 per cent solution of sodium hydroxide and the solution was heated on the water-bath for two hours. On cooling and standing for a short time the sodium salt of the β-camphoramidic acid, which had been formed, separated. The separation can be hastened by adding a little β-camphoramidic acid from a previous preparation, if that is available. The salt was filtered off, washed with a very little 10 per cent sodium hydroxide, dissolved in water, and the acid precipitated with hydrochloric acid. The acid can be most easily purified by dissolving it in a small amount of concentrated hydrochloric acid, filtering on

[1] *Loc. cit.*, p. 502.

[2] The work thus far was done by Mr. R. C. Warren.

[3] This JOURNAL, **26**, 286.

[4] *Ibid.*, **16**, 502.

asbestos, and precipitating by dilution with 2 or 3 volumes of water.

i-β-Camphoramidic acid, $C_8H_{14}\begin{cases}CO_2H\\CONH_2\end{cases}$, prepared as described, crystallizes in needles which melt at 178°. The active isomer melts at 182° to 183°.[1] 0.2011 gram of the acid required for its neutralization 10.28 cc. of N/10 potassium hydroxide. Theory requires 10.11 cc.

i-Dihydroaminocampholytic acid, $C_8H_{14}\begin{cases}CO_2H\\NH_2\end{cases}$, was prepared by exactly the same process used in the preparation of the active isomer.[2] It crystallizes in leaflets and so closely resembles the active body as scarcely to require a new description. The *chloroplatinate* is easily soluble. The *anhydride*, $C_8H_{14}\begin{cases}CO\\|\\NH\end{cases}$, melts at 188°, the same temperature as the melting-point of the anhydride of the active acid.[3]

i-Dihydrohydroxycampholytic Acid.—When the amino acid is treated with 0.5 molecule of sulphuric acid and 1 molecule of sodium nitrite it decomposes in a manner exactly similar to that of the decomposition of the active body,[4] yielding *i*-dihydrohydroxycampholytic acid and racemic *α*-campholytic acid. The hydroxy acid melted at 173°. The melting-point was given in our last paper as 176°, but a specimen of the old acid was now found to melt at 173°, and a mixture of the two acids melted at exactly the same temperature. The identity of the two is therefore beyond question. The melting-point here given was corrected by checking the thermometer with boiling aniline (183°.7).

The *i-α-campholytic acid* was obtained in small amount as a liquid. Its amide melted at 99°, the same temperature found for the melting-point of the amide of the acid prepared from *β*-campholytic acid, as described in our last paper, and a

[1] This JOURNAL, **16**, 310.
[2] *Ibid.*, **16**, 503.
[3] *Ibid.*, **16**, 504.
[4] *Ibid.*, **17**, 424.

mixture of the two amides melted at the same temperature.[1] Warming with dilute sulphuric acid (1 : 1) converts the acid into β-campholytic acid.

TERRE HAUTE, IND.,
April 2, 1902.

THE LOWERING OF THE FREEZING-POINT OF WATER PRODUCED BY CONCENTRATED SOLUTIONS OF CERTAIN ELECTROLYTES, AND THE CONDUCTIVITY OF SUCH SOLUTIONS.

BY HARRY C. JONES AND FREDERICK H. GETMAN.

We had hoped to carry this investigation much farther before publishing the results obtained, but a paper which has just appeared, by W. Biltz,[2] bearing upon the same subject, makes this preliminary publication necessary. Since the minimum in the molecular lowering of the freezing-point of water, produced by a large number of electrolytes, was discovered for most of these substances in this laboratory, and systematically studied for the first time by Jones and Chambers,[3] it seemed reasonable to expect that we would be given a fair amount of time to extend our investigations into this field which we had entered. This seemed all the more probable in that Jones and Chambers[4] stated at the close of the first investigation of this problem that "we propose to extend this investigation to a much larger number of hygroscopic substances, to ascertain whether there is any relation between this property and abnormal freezing-point lowerings, such as those recorded in this paper."

And Chambers and Frazer,[5] working with Jones, concluded their paper as follows: "It seems to us quite possible that work of the kind here described may help, if only a little,

[1] Blanc gives the melting-point as 103°. Our amide is evidently not quite pure, but when mixed with a sample of Dr. Blanc's amide, which he kindly sent us, the mixture melted at 101°. The two are, therefore, identical.

[2] Ztschr. phys. Chem., **40**, 185 (1902).

[3] This JOURNAL, **23**, 89 (1900).

[4] *Ibid.*, p. 105.

[5] *Ibid.*, **23**, 520 (1900).

towards the understanding of concentrated solutions, and we may thus be able to find out why it is that the laws which obtain for dilute solutions do not hold in the more concentrated. It is with this hope in mind that further work along the above line will be done."

The investigation, of which a preliminary account is here recorded, has for its object the study of a large number of electrolytes in water, to determine whether the minimum in the molecular lowering of the freezing-point was a general phenomenon, or whether it was manifested only by certain substances. We also desired to measure the freezing-point lowering produced by solutions of electrolytes of such great concentration that the ordinary Beckmann thermometer could not be employed. We, therefore, had two large Beckmann thermometers constructed. One of these had a range of 12° and was divided into fiftieths of a degree, and the other had a range of 25° and was divided into twentieths of a degree. The former was used for the more dilute solutions, the latter for the more concentrated. The apparatus employed was essentially that devised by Beckmann. The freezing-mixtures used in this work were sodium chloride and ice, and calcium chloride and ice. Several acids, one base, and a number of salts have been studied, as will be seen from the following results.

Column I. contains the concentrations of the solutions in terms of gram-molecular normal; II. is the observed lowering of the freezing-point of water; III., the correction due to the separation of ice; IV., the corrected lowering of the freezing-point; and V., the molecular lowering of the freezing-point.

In some cases two, in other cases three, determinations of the freezing-point of a solution were made. The mean of the several values is given in every case.

Hydrochloric Acid.

HCl (36.46).

I.	II.	III.	IV.	V.
1.0	4.130	0.012	4.118	4.118
1.0	4.150	0.025	4.125	4.125
			Mean,	4.122
1.5	6.690	0.066	6.620	4.413
1.5	6.750	0.108	6.640	4.427
			Mean,	4.420
2.0	10.160	0.304	9.860	4.928
2.0	10.275	0.257	10.018	5.009
			Mean,	4.969
2.5	13.550	....	13.550	5.420
2.5	13.470	0.055	13.420	5.370
			Mean,	5.400
3.0	18.100	0.004	18.096	6.030

Nitric Acid.

HNO_3 (63.05).

I.	II.	III.	IV.	V.
0.25	0.910	0.038	0.872	3.488
0.25	0.920	0.039	0.881	3.524
0.25	0.900	0.027	0.873	3.492
			Mean,	3.501
0.5	1.840	0.025	1.815	3.630
0.5	1.840	0.011	1.820	3.640
0.5	1.820	0.024	1.796	3.592
			Mean,	3.621
1.0	3.850	0.016	3.834	3.834
1.0	3.840	0.063	3.777	3.777
1.0	3.860	0.082	3.778	3.778
			Mean,	3.796
1.5	5.980	0.043	5.937	3.958
1.5	5.980	0.043	5.937	3.958
1.5	5.980	0.040	5.940	3.960
			Mean,	3.959

Nitric Acid (Continued).

I.	II.	III.	IV.	V.
	%	%	%	%
2.0	8.400	0.015	8.385	4.193
2.0	8.450	0.105	8.345	4.173
2.0	8.525	0.213	8.312	4.156
			Mean,	4.174
2.5	11.125	0.060	11.065	4.426
2.5	11.125	0.078	11.047	4.418
2.5	11.125	0.099	11.026	4.410
			Mean,	4.418
3.0	13.950	0.279	13.671	4.557
3.0	14.150	0.071	14.079	4.693
3.0	14.075	0.099	13.976	4.659
			Mean,	4.603

Sulphuric Acid.

H_2SO_4 (98.08).

I.	II.	III.	IV.	V.
	%	%	%	%
0.1	0.415	0.017	0.398	3.980
0.1	0.412	0.016	0.396	3.960
0.1	0.411	0.015	0.396	3.960
			Mean,	3.970
0.2	0.820	0.003	0.817	4.090
0.2	0.820	0.003	0.817	4.090
0.2	0.820	0.002	0.818	4.090
			Mean,	4.090
0.3	1.190	0.022	1.168	3.890
0.3	1.180	0.005	1.175	3.920
0.3	1.200	0.024	1.176	3.920
			Mean,	3.910
0.4	1.600	0.020	1.580	3.950
0.4	1.610	0.022	1.588	3.970
0.4	1.640	0.030	1.610	4.020
			Mean,	3.980
0.5	2.040	....	2.040	4.080
0.5	2.040	....	2.040	4.080
0.5	2.040	0.023	2.017	4.030
			Mean,	4.060

Sulphuric Acid (Continued).

I.	II.	III.	IV.	V.
1.0	4.210	0.019	4.191	4.191
1.0	4.200	0.006	4.194	4.194
1.0	4.200	0.016	4.184	4.184
			Mean,	4.190
1.5	7.450	0.008	7.442	4.961
1.5	7.450	0.006	7.444	4.963
1.5	7.450	0.008	7.442	4.961
			Mean,	4.962
2.0	11.325	0.005	11.320	5.660
2.0	11.300	0.005	11.295	5.648
2.0	11.275	0.002	11.273	5.637
			Mean,	5.648
2.5	16.275	....	16.275	6.510

Potassium Hydroxide.

KOH (56).

I.	II.	III.	IV.	V.
0.2	0.730	0.005	0.725	3.630
0.2	0.723	0.009	0.714	3.570
0.2	0.728	0.009	0.719	3.600
			Mean,	3.600
0.5	1.820	0.022	1.798	3.596
0.5	1.810	0.002	1.808	3.616
0.5	1.810	0.002	1.808	3.616
			Mean,	3.609
1.0	3.920	0.045	3 875	3.875
1.0	3.940	0.031	3.909	3.909
1.0	3.920	0.034	3.886	3.886
			Mean,	3.890
1.5	5.975	0.013	5.962	3.975
1.5	5.975	0.010	5.965	3.977
1.5	5.975	0.010	5.965	3.977
			Mean,	3.976

Potassium Hydroxide (*Continued*).

I.	II.	III.	IV.	V.
2.0	8.475	0.007	8.468	4.234
2.0	8.450	0.003	8.447	4.224
2.0	8.550	0.009	8.541	4.270
			Mean,	4.243
2.5	11.375	0.009	11.366	4.546
2.5	11.300	0.005	11.295	4.518
2.5	11.250	0.004	11.246	4.498
			Mean,	4.521

Calcium Chloride.

$CaCl_2$ (110.8).

I.	II.	III.	IV.	V.
0.5	2.740	0.002	2.738	5.476
0.5	2.730	0.002	2.728	5.456
0.5	2.750	0.007	2.743	5.486
			Mean,	5.473
1.0	6.350	0.008	6.342	6.342
1.0	6.350	0.002	6.348	6.348
1.0	6.330	0.006	6.324	6.324
			Mean,	6.338
1.5	11.300	0.004	11.296	7.531
1.5	11.325	0.005	11.320	7.547
1.5	11.300	0.004	11.296	7.531
			Mean,	7.536
2.0	17.975	0.002	17.973	8.987
2.0	17.875	0.008	17.867	8.934
2.0	17.875	0.008	17.867	8.934
			Mean,	8.952

Strontium Chloride.

$SrCl_2$ (158.5).

I.	II.	III.	IV.	V.
0.5	2.620	0.005	2.615	5.230
0.5	2.630	0.008	2.622	5.244
0.5	2.610	0.005	2.605	5.210
			Mean,	5.228

Strontium Chloride (*Continued*).

I.	II.	III.	IV.	V.
1.0	6.060	0.017	6.043	6.043
1.0	5.960	....	5.960	5.960
1.0	6.010	0.003	6.007	6.007
			Mean,	6.003
1.5	10.825	0.005	10.820	7.213
1.5	10.725	....	10.725	7.150
1.5	10.725	....	10.725	7.150
			Mean,	7.171
2.0	16.450	0.005	16.445	8.223
2.0	16.425	0.003	16.422	8.211
2.0	16.425	0.003	16.422	8.211
			Mean,	8.215

Barium Chloride.

$BaCl_2$ (208.3).

I.	II.	III.	IV.	V.
0.25	1.230	0.001	1.229	4.916
0.25	1.270	0.046	1.224	4.900
0.25	1.230	0.001	1.229	4.916
			Mean,	4.911
0.50	2.550	0.024	2.526	5.052
0.50	2.500	0.007	2.493	4.986
0.50	2.550	0.030	2.520	5.040
			Mean,	5.023
0.75	4.010	0.003	4.007	5.343
0.75	3.860	0.005	3.855	5.140
0.75	3.860	0.001	3.859	5.145
			Mean,	5.209

Sodium Nitrate.

$NaNO_3$ (85.09).

I.	II.	III.	IV.	V.
0.05	0.200	0.001	0.199	3.980
0.05	0.205	0.002	0.203	4.060
0.05	0.195	0.002	0.193	3.860
			Mean,	3.967

Sodium Nitrate (*Continued*).

I.	II.	III.	IV.	V.
0.1	0.370	....	0.370	3.700
0.1	0.370	0.002	0.368	3.680
0.1	0.355	....	0.355	3.550
			Mean,	3.643
0.2	0.710	0.001	0.709	3.545
0.2	0.730	0.030	0.700	3.500
0.2	0.710	....	0.710	3.550
			Mean,	3.532
0.3	1.050	0.001	1.049	3.497
0.3	1.045	0.010	1.035	3.450
0.3	1.035	....	1.035	3.450
			Mean,	3.468
0.4	1.350	0.001	1.349	3.372
0.4	1.350	0.002	1.348	3.370
0.4	1.350	0.003	1.347	3.368
			Mean,	3.370
0.5	1.670	0.001	1.669	3.338
0.5	1.675	0.001	1.674	3.348
0.5	1.675	0.001	1.674	3.348
			Mean,	3.345
1.0	3.220	....	3.220	3.220
1.0	3.200	0.003	3.197	3.197
1.0	3.200	0.001	3.199	3.199
			Mean,	3.205
1.5	4.670	0.001	4.669	3.113
1.5	4.690	....	4.690	3.127
1.5	4.650	....	4.650	3.100
			Mean,	3.113
2.0	6.150	0.004	6.146	3.073
2.0	6.150	0.002	6.148	3.076
2.0	6.110	....	6.110	3.055
			Mean,	3.068

Sodium Nitrate (Continued).

I.	II.	III.	IV.	V.
2.5	7.450	0.004	7.446	2.978
2.5	7.470	0.002	7.468	2.987
2.5	7.490	....	7.490	2.996
			Mean,	2.987
3.0	8.913	0.005	8.908	2.969
3.0	8.913	0.003	8.910	2.970
3.0	8.830	0.004	8.826	2.942
			Mean,	2.960

Potassium Nitrate.

KNO_3 (101.19).

I.	II.	III.	IV.	V.
0.05	0.195	0.001	0.194	3.880
0.05	0.195	....	0.195	3.900
0.05	0.195	....	0.195	3.900
			Mean,	3.893
0.1	0.360	0.001	0.359	3.590
0.1	0.365	0.002	0.363	3.630
0.1	0.370	0.004	0.366	3.660
			Mean,	3.627
0.2	0.680	0.023	0.657	3.285
0.2	0.675	0.001	0.674	3.370
0.2	0.670	0.001	0.669	3.345
			Mean,	3.333
0.3	0.985	0.002	0.983	3.277
0.3	1.010	0.038	0.972	3.240
0.3	0.985	0.001	0.984	3.280
			Mean,	3.266
0.4	1.270	....	1.270	3.175
0.4	1.290	....	1.290	3.225
0.4	1.295	0.037	1.258	3.145
			Mean,	3.182

Potassium Nitrate (Continued).

I.	II.	III.	IV.	V.
0.5	1.580	0.030	1.550	3.100
0.5	1.550	....	1.550	3.100
0.5	1.530	0.002	1.528	3.056
			Mean,	3.085
1.0	2.730	0.001	2.729	2.729
1.0	2.740	0.002	2.738	2.738
1.0	2.730	....	2.730	2.730
			Mean,	2.732

An examination of the above tables will show that a minimum exists in the molecular lowering of the freezing-point of all the acids, the base, and all the salts studied with the exception of two. In potassium nitrate and sodium nitrate the molecular lowering decreases with the concentration from the most dilute to the most concentrated solution studied, showing no trace of a minimum at any dilution. These facts will be shown more clearly when the results are plotted as curves, which will be done when the work is published in full.

Having found a minimum in the molecular lowerings of the freezing-point of water as produced by such a number of electrolytes, we determined to study the molecular conductivity of concentrated solutions of these substances, especially at those concentrations where the freezing-point minimum manifested itself.

The resistance to the passage of the current offered by such concentrated solutions is so small that a special form of cell was constructed, in which the plates were not large, and placed a considerable distance apart. This cell will be described more in detail in a later publication.

The results obtained are given in the following tables. v represents the volume of the solution; μ_0° the molecular conductivities of the solutions at zero degrees:

Hydrochloric Acid.

v.	$\mu_v 0°$.
1.000	200.32
0.667	182.35
0.500	170.19
0.400	152.38
0.333	141.87

Nitric Acid.

v.	$\mu_v 0°$.
1.000	194.95
0.667	184.89
0.500	169.23
0.400	155.43
0.333	140.97

Sulphuric Acid.

v.	$\mu_v 0°$.
1.000	253.44
0.667	221.25
0.500	199.42
0.400	178.79
0.333	155.29
0.286	135.00
0.250	118.86
0.222	100.21
0.200	86.97

Potassium Hydroxide.

v.	$\mu_v 0°$.
1.000	113.33
0.667	106.35
0.500	101.15
0.400	97.40

Calcium Chloride.

v.	$\mu_v 0°$.
1.000	71.16
0.667	62.14
0.500	53.98
0.400	44.79

Barium Chloride.

v.	$\mu_v 0°$.
20.000	116.05
10.000	103.79
4.000	95.94
2.000	89.24
1.333	85.27

Strontium Chloride.

v.	$\mu_v 0°$.
2.000	84.26
1.000	74.57
0.667	63.01
0.500	55.26

Sodium Nitrate.

v.	$\mu_v 0°$.
1.000	40.41
0.667	36.90
0.500	34.16
0.400	30.96

Potassium Nitrate.

v.	$\mu_v 0°$.
1.000	49.97
0.667	46.30

The molecular conductivities increase in every case regularly with the dilution, showing no sign of a minimum at any concentration.

We shall not discuss these results in this connection, but reserve any theoretical considerations for a later and fuller publication.

We wish to state that we are extending these investigations to a much larger number of electrolytes, and to a number of solvents, along the lines which we have been investigating in this laboratory.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
April, 1902.

ACTION OF PHOSPHORUS PENTACHLORIDE ON ANILINE.

BY J. ELLIOTT GILPIN.

In a previous paper in this JOURNAL[1] several products formed by the action of phosphorus pentachloride on aniline and its salts were described. It was shown that phosphorus pentachloride and aniline hydrochloride, when heated together, formed a compound whose composition could be represented by the formula $PCl_5(C_6H_5N)$, while the substance formed when the chloride is treated with aniline itself, at ordinary temperatures, was $PCl(C_6H_5NH)_4$. The amount of carbon in the latter compound could not be determined by the usual method, as the substance, when heated, was partly changed into a black mass which still contained carbon, but in an extremely stable form. Efforts have been made to determine the exact nature of this substance, but the results obtained lead to the conclusion that it is not a single definite substance but a mixture. When the compound

$$PCl(C_6H_5NH)_4$$

is heated it is decomposed, forming aniline and other products which escape as gases, and a black porous mass resembling coke. If this black residue is heated red hot, in a porcelain crucible, it slowly volatilizes with decomposition, but the mass shows no tendency to melt, even at that temperature, and the separate particles remain dry and retain their individual form.

[1] This JOURNAL, 19, 352.

When the crucible was heated directly in the flame of the burner so that the gases present in the flame enveloped the crucible, a flame similar to that of burning phosphorus was observed around the edge of the crucible, and a cover placed on it soon became covered on the inside with an oily liquid which proved to be phosphoric acid. Further experiment showed that the oxide of phosphorus, formed by the burning of the phosphorus which had been set free, combined with the water vapor in the flame to form the acid found. In order to avoid contact of the gases in the flame with the contents of the crucible, the latter was placed in a circular opening in an asbestos board which allowed the substance to be heated without being enveloped in the flame. This led to a more thorough study of the substance and its decomposition-products, in the course of which it was shown that besides phosphorus, nitrogen, hydrogen, and carbon were also present, but that specimens of the same original substance, when heated for different lengths of time, showed lack of uniformity and difference of composition.

When the substance was heated in a small porcelain tube in a stream of dry nitrogen, ammonia and a volatile substance, with an odor very similar to that of isocyanides, passed off as gases, while a very light-yellow powder, which was pure phosphorus, collected in the front end of the porcelain tube and in the condenser connected with it. Similar products were also formed when dry carbon dioxide gas was used instead of nitrogen, although apparently not so readily.

The phosphorus could be determined quantitatively by oxidation with potassium hydroxide and potassium nitrate and precipitation as ammonium magnesium phosphate, and the nitrogen by the Gunning modification of the Kjeldahl method. The percentage of nitrogen dropped from 8.87 to 8.16 and then to 7.38 per cent in successive specimens taken after heating the previous one for from fifteen to twenty minutes.

Besides the substances mentioned above, two compounds whose composition can be expressed by the formulas

$P(NC_6H_5)_2(NHC_6H_5)$ and $P_2Cl(NHC_6H_5)_7$

have been obtained by the action of aniline on phosphorus pentachloride under different conditions.

All efforts to replace the last chlorine atom in the pentachloride by the anilide group to form $P(NHC_6H_5)_5$ have failed. Up to the present time no conditions have been found under which all five of the chlorine atoms could be replaced by anilide residues nor could the chlorine atom in

$$PCl(NHC_6H_5)_4$$

be replaced by the aniline residue. There was no action when the $PCl(C_6H_5NH)_4$ was heated in a sealed tube with aniline alone or with aniline and some substance which would combine with the chlorine. Jackson and Mencke met with a similar difficulty in their investigation of the action of phosphorus trichloride on aniline and were also unable to replace the last chlorine atom.

The relationship to phosphorus pentachloride of the substances thus far described can be expressed by the following formulas:

PCl_5, $PCl_3(C_6H_5N)$, $PCl(C_6H_5NH)_4$,
$P(C_6H_5N)_2(C_6H_5NH)$, $P_2Cl(C_6H_5NH)_7$.

Preparation of $P(NC_6H_5)_2(NHC_6H_5)$.

About 10 grams of aniline were dissolved in 250 cc. of benzene and an equal quantity of benzene was saturated, at the ordinary temperature, with phosphorus pentachloride. Both solutions were then well cooled and were kept so while the solution of the pentachloride was slowly added to the aniline solution. After standing for some hours, the aniline hydrochloride, which had separated out, was filtered off and the product, obtained by the slow evaporation of the benzene, was washed with boiling water, in which it is entirely insoluble, to remove any soluble phosphorus compounds and most of the benzene, and then crystallized from alcohol. The substance thus obtained formed clear, well-defined crystals, which contain no water of crystallization and melt sharply at 208° to

210° (uncorr.). They belong to the orthorhombic system and show the following faces:

$$o = OP; \quad e = P; \quad m = \infty P\breve{2}; \quad b = \infty P\breve{\infty}.$$

The axial ratio is a : b : c = 0.27956 : 1 : 0.258614 and the values of the angles are as follows:

$$o \wedge e = 134° 2';$$
$$e \wedge e' = 95° 57';$$
$$e \wedge e = 158° 34';$$
$$m \wedge m = 121° 30';$$
$$m \wedge b = 119° 15';$$
$$m \wedge e = 132° 37'.$$

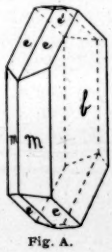


Fig. A.

This substance also crystallizes in tufts of soft, hair-like needles. The form which the crystals take is dependent upon the conditions under which the substance separates from the solution. It is, like the other substances described in these articles, quite stable and resists the action of many reagents. There is no action when it is heated with water in a sealed tube for six hours at 175° nor when heated with alcoholic potash. Aqueous potash and concentrated hydrochloric acid do not act on it, but concentrated sulphuric acid decomposes it with the formation of sulphanilic acid. Fuming nitric acid also decomposes it. An analysis of the substance gave the following results:

0.2267 gram substance gave 0.030557 gram N.
0.3469 gram substance gave 0.046082 gram N.

0.2398 gram substance gave 0.032845 gram N.
0.2537 gram substance gave 0.034127 gram N.
0.2423 gram substance gave 0.033503 gram N.
0.1647 gram substance gave 0.0588 gram $Mg_2P_2O_7$.
0.1871 gram substance gave 0.0688 gram $Mg_2P_2O_7$.
0.1642 gram substance gave 0.0575 gram $Mg_2P_2O_7$.
0.0640 gram substance gave 0.0225 gram $Mg_2P_2O_7$.

	Calculated for $P(NC_6H_5)_2(NHC_6H_5)$.	Found. I.	II.	III.	IV.	V.
N	13.77	13.47	13.28	13.69	13.41	13.82
P	10.16	....	9.92	10.27	9.78	9.82

As the same difficulty was encountered, in efforts to determine the amount of carbon and hydrogen, as in the other case mentioned above, the composition, as calculated from the results of the determination of nitrogen and phosphorus, was confirmed by determinations of the molecular weight made by the boiling-point method, using alcohol as a solvent.

Alcohol. Grams.	Substance. Grams.	Rise in boiling-point.	Molecular weight.
54.475	0.8887	0°.062	302
61.279	1.8948	0°.128	278
63.338	1.6767	0°.102	335
57.805	0.8622	0°.056	306
57.805	1.3023	0°.087	298
		Mean,	303.8
Calculated for $P(NC_6H_5)_2(NHC_6H_5)$			305

Preparation of $P_2Cl(NHC_6H_5)_7$.

By the method used for the preparation of the chlorphostetranilide ($PCl(NHC_6H_5)_4$), which consisted in adding phosphorus pentachloride to aniline at the ordinary temperature, washing the product with boiling water, and, after drying, extracting any easily soluble matter with cold alcohol, a few well-defined crystals were often obtained when the solution was allowed to evaporate slowly. These crystals had bright faces and sharp angles when first removed from the solution, but upon exposure to the air rapidly became dull, and finally crumbled to a powder. Although aniline and phosphorus

pentachloride have been brought together in various proportions and under different conditions of temperature, in order to produce this substance in quantity it has, so far, been impossible to find any conditions under which it is formed as anything more than a by-product in very small quantities.

The best yield is obtained when phosphorus pentachloride is added to boiling aniline as long as any action takes place, but even then the yield is very small, only a few crystals being formed when as much as 50 grams of aniline are used. As the formation of this substance has never been noticed when phosphorus pentachloride acts on the aniline in a cold solution, but only when the action takes place at high temperatures, it would suggest the possibility of the action being more complete if the substances could react at high temperatures. As, however, phosphorus pentachloride acts on aniline to form $PCl(NHC_6H_5)_4$ as soon as they come in contact, and further treatment with excess of either substance produces no action, the possibility of controlling the conditions so as to increase the yield of the desired product seems very slight.

After the solid, formed by the action of the phosphorus pentachloride on the boiling aniline, has cooled it is broken up and boiled with water to remove all excess of phosphorus compounds or aniline. The powdered and dry substance is then treated with a little cold alcohol which, if it is allowed to act for only a short period, dissolves out all of the easily soluble by-product, but only a small amount of the other product, which is present in very large excess.

The crystals which are formed by the slow evaporation of this solution are picked out, washed with alcohol, and dried. It is necessary to pick out each crystal and wash it with alcohol to remove the other substance, which separates out first and often sticks to the large crystals. One extraction with cold alcohol serves to remove all of the substance present in the mass. The crystals must be kept in a closed vessel over alcohol in order to preserve the luster of the faces as a few minutes' contact with the air sometimes makes them dull,

owing to the loss of the alcohol present as alcohol of crystallization. The powder obtained by driving out the alcohol melts at 192° to 194°. The substance crystallizes in the monoclinic system and exhibits a hemihedral habit. The following constants were calculated from the interfacial angles of the unit hemi-pyramids and unit prisms:

$$\beta = 87° 28'. \quad a : b : c = 1.32375 : 1 : 0.55845.$$

Planes observed:

p (111, —P),
o ($11\bar{1}$, P),
a (100, $\infty P\bar{\infty}$),
b (010, $\infty P\breve{\infty}$),
m (110, ∞P),
x (221, 2P) probably,
z (120, $\infty\breve{P}2$) probably.

It exhibits a perfect cleavage parallel to the orthopinacoid $\infty P\bar{\infty}$ (100) and an imperfect one parallel to an orthodome, probably $2P\bar{\infty}$ (201). Penetration twins were observed in a number of cases, the twinning planes being either the clinoprism $\infty\breve{P}2$ (120) or the orthodome $2P\bar{\infty}$ (201).

The table on opposite page represents the results of a number of measurements:[1]

The following figures illustrate the different habits and twinning laws observed on the crystals:

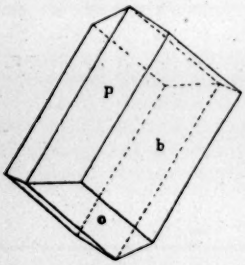


Fig. I.

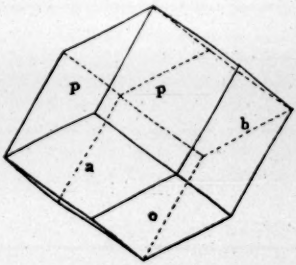


Fig. II.

[1] I am indebted to Mr. A. C. Spencer for the crystallographic measurements.

Angle.	Crystal No. 1.	Crystal No. 2.	Crystal No. 3.	Crystal No. 4.	Crystal No. 5.	Crystal No. 6.	Crystal No. 7.	Crystal No. 8.	Crystal No. 9.	Crystal No. 10.	Average values.	Calculated values.	Variation.
o : p	40°31½′	40°25′	40°13′	40°13½′	40°32′	40°11½′	40°25½′	40°13′	....	....	40°20′45″	40°25′55″	+5′10″
o : o	....	....	....	....	....	54°½′	53°33′	....	....	53°46′	53°39′30″	....	....
p : p	....	....	....	....	....	56°8′	55°20′	....	55°29′	....	55°39′00″	....	....
p : a	....	....	....	....	....	71°18′	71°47′	....	71°41′	....	71°44′00″	71°43′59″	—00′1″
p : b	....	....	....	....	....	....	61°53′	62°33′	62°17′	....	62°25′00″	62°25′00″	00
o : b	....	....	....	....	....	....	63°23½′	....	63°22′	....	63°23′00″	63°10′00″	—13′00″
o : a	67°52′	....	....	....	....	....	....	....	....	....	67°52′00″	67°50′6″	—1′54″
m : b	36°25½′	....	....	....	....	....	....	....	....	....	36°25′30″	37°5′43″	+40′13″
m : a	53°35½′	53°11′	53°25′	....	....	....	....	....	....	....	53°23′50″	52°54′17″	—29′33″
o : m	55°4′	....	....	....	....	....	....	....	....	54°30′	54°47′00″	55°31′54″	+44′54″
p : m	....	....	....	....	53°43′	....	....	....	....	53°56′	53°49′30″	54°31′38″	+42′8″

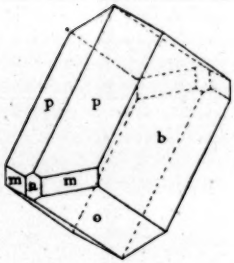


Fig. III.

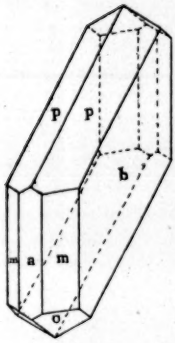


Fig. IV.

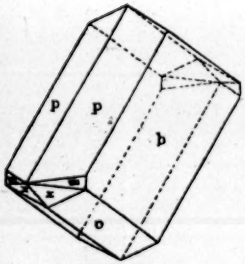


Fig. V.

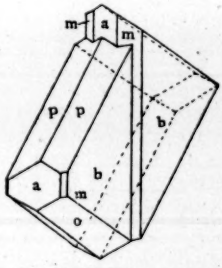


Fig. VI.

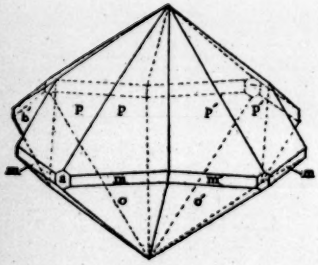


Fig. VII.

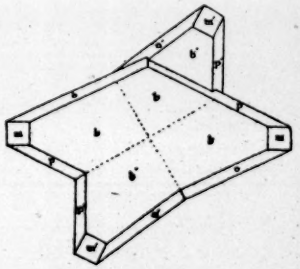


Fig. VIII.

Fig. I. shows the combination of the two hemi-pyramids with the clinopinacoid, while Fig. II. contains in addition the orthopinacoid. The equal development of the pyramids, pinacoids, and prisms gives a combination closely resembling in appearance the rhombic dodecahedron of the regular system. Figs. III. and IV. represent crystals which are alike in type but different in habit. Fig. V. represents a crystal which is tabular parallel to the clinopinacoid and in which the faces *b* and *a* are very slightly developed. In some cases, as in Fig. VI., a faulted appearance is noted and sometimes one half is smaller than the other and is placed on the face (*a*).

In Fig. VII. individuals twinned parallel to the clinoprism $\infty P2(120)$ are represented, and in Fig. VIII. a projection of a twin with the orthodome $2P\overline{\infty}(201)$ as the twinning plane.

Analyses of a number of specimens of the substance gave the following results:

0.8657 gram substance lost, on heating, 0.0864 gram = 9.98 per cent.

0.3325 gram substance lost, on heating, 0.0344 gram = 10.34 per cent.

0.2026 gram substance lost, on heating, 0.0215 gram = 10.61 per cent.

0.392 gram substance lost, on heating, 0.0406 gram = 10.35 per cent.

0.4873 gram substance lost, on heating, 0.0514 gram = 10.54 per cent.

0.5121 gram substance lost, on heating, 0.0531 gram = 10.36 per cent.

0.1715 gram substance gave 19.55 cc. N at 19° and 768.9 mm. pressure.

0.335 gram substance gave 39.7 cc. N at 20°.5 and 763.2 mm. pressure.

0.1449 gram substance gave 16.9 cc. N at 11° and 763 mm. pressure.

0.1887 gram substance gave 23.3 cc. N at 19°.5 and 755 mm. pressure.

0.2878 gram substance gave 33.6 cc. N at 18°.5 and 758.6 mm. pressure.

0.1825 gram substance gave 0.0321 gram AgCl.
0.132 gram substance gave 0.0265 gram AgCl.
0.1752 gram substance gave 0.035 gram AgCl.
0.1571 gram substance gave 0.0262 gram AgCl.
0.2285 gram substance gave 0.0367 gram AgCl.
0.1406 gram substance gave 0.0423 gram $Mg_2P_2O_7$.
0.1656 gram substance gave 0.0502 gram $Mg_2P_2O_7$.
0.2733 gram substance gave 0.0822 gram $Mg_2P_2O_7$.
0.159 gram substance gave 0.048 gram $Mg_2P_2O_7$.
0.2064 gram substance gave 0.0633 gram $Mg_2P_2O_7$.
0.0882 gram substance gave 0.2186 gram CO_2.
0.113 gram substance gave 0.2788 gram CO_2.
0.1336 gram substance gave 0.3364 gram CO_2.
0.1012 gram substance gave 0.2537 gram CO_2.
0.1336 gram substance gave 0.0747 gram H_2O.
0.2506 gram substance gave 0.1275 gram H_2O.

	Calculated for $P_5Cl(NHC_6H_5)_7$.	Found.				
P	8.36	8.37	8.44	8.40	8.43	8.57
N	13.22	13.26	13.12	13.96	14.06	13.43
Cl	4.77	4.34	4.96	4.98	4.12	3.97
C	67.98	67.58	67.28	68.66	68.36	....
H	5.67	6.21	5.65	....	....	....

	Calculated for $P_5Cl(NHC_6H_5)_7+2C_2H_5OH$.	Found.					
C_2H_5OH	11.03	9.98	10.34	10.61	10.35	10.54	10.36

The low results obtained in the determination of the loss of alcohol of crystallization were probably due to loss while the crystals were being dried and powdered for heating, as they lose the alcohol very rapidly in contact with air. That the substance given off was alcohol was clearly shown by collecting the liquid and testing for alcohol.

While this material is easily dissolved out of the original mixture by a little cold alcohol, the powder obtained by dehydrating the crystals is only very slightly soluble in cold alcohol and, from the experiments made, appears to change to $PCl(NHC_6H_5)_4$ when boiled with alcohol so that it is impossible to purify the substance by recrystallization.

JOHNS HOPKINS UNIV.,
April, 1902.

Contributions from the Sheffield Laboratory of Yale University.

XCV.—THE PERIODIC SYSTEM AND THE PROPERTIES OF INORGANIC COMPOUNDS.

IV.—THE SOLUBILITY OF DOUBLE SULPHATES OF THE FORMULA $M^{I}_{2}M^{II}(SO_4)_2.6H_2O$.

By James Locke.

In continuation of the plan laid out, of systematically examining, under the same conditions, the properties of analogous inorganic compounds[1] to ascertain by direct experiment what the influence of change in the atomic weights of their variable constituents may be, I wish in this paper to give the results of a study of the solubilities of the double sulphates of bivalent metals.

The series of isomorphous salts of the general formula

$$M^{I}_{2}M^{II}(SO_4)_2.6H_2O$$

is an unusually extensive one. M^{I} may be any alkali metal except sodium and lithium, the double sulphates of which, with bivalent metals, either contain less water of crystallization than is indicated in the above formula, or do not exist at all.[2] The place of the alkali metal may also be filled by ammonium and thallium. As representatives of M^{II} we have three members of the second family in the periodic system, magnesium, zinc, and cadmium, and also the three lightest metals in the eighth family, iron, nickel, and cobalt; also two metals, manganese and copper, the positions of which in the system are adjacent to the above. The series thus forms an especially convenient means of studying:

1. The gradations in solubility of compounds of metals which are members of the same group in the system.

2. The relative solubility of compounds formed by elements adjacent in position to those for which such compounds conform to the degree of valence required by the system.[3]

[1] This Journal, **20**, 581; **26**, 166, 332.

[2] It is doubtful whether any lithium salts at all can be obtained.

[3] For instance, copper, which is adjacent to zinc, the normal valence of which, according to the periodic system, is two, while that of copper is one.

3. The relative solubility of compounds of an element (Tl) the position of which is in every respect far removed from those of its analogues; and

4. The relative behavior of the compounds of a complex radical.

A similar investigation of the alums of aluminium, vanadium, chromium, and iron, touched, so far as the trivalent metals were concerned, only the second of these points. It was found that there was no steady increase or decrease in solubility with ascending atomic weights. The order of increasing solubilities was the same for the salts of all the univalent metals, and ran:

$$Al \rightarrowtail Cr \rightarrowtail V \rightarrowtail Fe,$$

while that of the atomic weights is

$$Al \rightarrowtail V \rightarrowtail Cr \rightarrowtail Fe.$$

Among the alkali metals proper, the order of solubility,

$$Cs \rightarrowtail Rb \rightarrowtail K \rightarrowtail Na,$$

was uninfluenced by the nature of the trivalent metal, but was the reverse of that of the atomic weights. This, however, did not extend to the compounds of thallium, which in its position in the system is far removed from the alkali metals. The thallium salts all fell between those of potassium and rubidium, instead of at the end of the series. The ammonium salts, too, lay between those of rubidium and potassium, so the low molecular weight of the NH_4 radical finds no expression in the solubility of its salts. The complete order found for M^I was

$$Cs \rightarrowtail Rb \rightarrowtail Tl \rightarrowtail NH_4 \rightarrowtail K \rightarrowtail Na.$$

Potassium and sodium alums could be obtained only with such trivalent metals as yield the most sparingly soluble alums. The compounds Na–Fe, Na–Ga, Na–In, K–Ga, and K–In do not exist. The question arises as to whether this is due simply to the fact that such compounds would be too soluble to permit of their isolation, or to an actual difference between these metals and caesium, etc., in their power to enter into such compounds. A difference in the tendency of differ-

ent metals of a group to enter into compounds of the same general formula has not been generally recognized in the literature, and when noticed, it has usually been regarded as due simply to difference in solubility. There can be no doubt, however, but that such tendency is specific and plays a very important part in the formulas of the compounds of analogous elements. In the double sulphates with the bivalent metals, as will be seen, it can be very sharply traced.

The order of solubilities in this series stands even more in conflict with the periodic system than does that found for the alums. In answer to the above-mentioned points the data indicate that:

1. The compounds of metals in the same family of the periodic system do not follow the same or the reverse order of their atomic weights. This is true in each of the three natural groups of metals contained in the series.

2. No correlation can be found between the solubilities of the manganese and cupric salts, and the "adjacent positions" of these elements in the system.

3. The solubilities of the thallium salts cannot be interpreted through a consideration of that element's position, which is far removed from those of the alkali metals.

4. The influence of each alkali metal upon the solubility of its compounds is specific and retained throughout all of them. The same is true of the salts of ammonium. While conforming neither to the atomic weights of the elements nor to the molecular weights of the compounds, the solubilities stand in simple mathematical relation to one another, and that of any compound can be calculated from the constants representing the specific influence of the two metals which it contains. This being also true for the ammonium salts, it follows that in any system by which the inorganic compounds are to be exactly classified, the basis must be something which is as applicable to the salts of a compound radical as to an element, and which therefore cannot be the atomic weights, for these are limited to the elements alone.

In drawing this conclusion I do not wish to appear to attach too much importance to so simple a property as solubility, nor as suggesting that any system of classification be

based upon such a property alone. My results are simply an indication in a field which, except in crystallography, has been left almost untouched. The inorganic literature does not to-day contain a single instance in which complete, comparable data are at hand for all members of a series of homologous compounds, in measurement of solubility, degree of dissociation, melting-points, stability, or any other property. If we have any underlying distrust of the periodic system, it certainly does not appear to a marked extent in the literature, for except in rearrangements which leave the vital discrepancies as conspicuous as before, there has been not one attempt to correct it. To-day we know almost absolutely nothing of the gradations of properties in homologous inorganic series, except in the way of merely qualitative observations from as many different standpoints as there have been investigators of the subject. There is, then, no real possibility of extending the periodic system, or of obtaining a satisfactory new basis of classification, until quantitative data are at hand by which to judge its applicability. In the desire to ascertain how exactly gradation can be traced, I have undertaken this series of investigations, and have chosen solubility as the first property to be examined, simply because it is the most easily determined. There is probably no other one property, however, from which more information can be derived. For if a simple relation exists between the solubilities in a homologous series of hydrated double salts, then it probably follows that the same is true of the vapor-tension of their crystals, of the degree of their molecular dissociation, of the ionic dissociation of their analogous constituents, and of other properties upon which solubility presumably depends.

The methods employed for determining the solubilities was that described in my first article on the alums. The saturated solutions were evaporated to dryness at 100°, and then heated to 150° to 200° until the weight of the residual salts remained constant. This usually required about four hours. The accuracy of the method was first ascertained on a large variety of salts. In some cases the results were further confirmed by sulphuric acid determinations, or, in the case of the ammonium salts, by ignition. The ferrous salts were estima-

ted by titration with potassium permanganate. Special precautions were taken, in the case of these salts, to prevent oxidation. The dried salts were introduced into the bottles, into which a rapid current of carbon dioxide was then led, and the salts vigorously shaken to expel all air. Without turning off the current, the salts were then covered with water which had been boiled a long time, and the bottles finally quickly corked. The caesium and rubidium material used was tested from time to time by the spectroscope.

Below I give the solubilities of all the salts of the group, the data for which admit of comparison. The temperature throughout was 25°, and constant within 0°.1. In Table I. the numbers express the parts by weight of the anhydrous salts dissolved in 1 liter of water. Table II. gives the number of gram-molecules per liter, calculated from the formula

$$\frac{W}{M(a-W)},$$

in which W is the weight of the dissolved salt, a that of the solution, and M the molecular weight of the anhydrous salt. The atomic weights used in the calculations were: K, 39.15; Rb, 85.4; Cs, 133; NH_4, 18; Tl, 204.1; Mg, 24.36; Mn, 55.0; Fe, 56.0; Ni, 58.7; Co, 59.0; Cu, 63.6; Zn, 65.4; Cd, 112.0. The solubilities given represent in each case the mean of from three to six determinations, on as many different preparations. For the more sparingly soluble salts the error is probably not more than 0.002 gram-molecule per liter; for the caesium salts it is very slightly greater.

Table I.—Parts Per Liter of Water.

	Mg.	Mn.	Fe.	Ni.	Co.	Cu.	Zn.	Cd.
Tl	...	...	...	46.1	...	81	86.0	...
Rb	202	357	242	59.8	92.8	102.8	101.0	767
K	...	...	...	68.8	128.8	116.9	131.9	...
NH_4	199	372	351	75.7	147.2	....	140.8	723
Cs	533	804	1011	255.8	418.8	460.0	386.3	1399

Table II.—Gram-Molecules Per Liter.

	Mg.	Mn.	Fe.	Ni.	Co.	Cu.	Zn.	Cd.
Tl	....	....	....	0.070	....	0.122	0.129	....
Rb	0.521	0.857	0.579	0.142	0.220	0.241	0.236	1.615
K	....	....	....	0.209	0.391	0.350	0.393	....
NH	0.791	1.321	1.044	0.264	0.513	....	0.480	2.125
Cs	1.106	1.570	1.967	0.495	0.810	0.882	0.738	2.455

Comparative researches upon this series of salts have up to the present time been confined almost entirely to the study of their crystallography. A few solubility determinations have been made upon individual compounds of the series, at different temperatures, but only one approximately thorough investigation of the subject is recorded. This was the work of Tobler,[1] who, to quote his own words, wished to ascertain "the effect caused by the substitution of an alkali sulphate for the seventh molecule of water in the vitriols, $MSO_4.7H_2O$." Needless to say, no relation between the solubilities of the simple salts and double salts could be traced. A careful examination of Tobler's work shows that his results are not very trustworthy. He finds, for instance, that the double salts containing ammonium are in every case less soluble than the corresponding potassium compounds. My own results very positively show the reverse. Our results for the ammonium salts do not differ to any great extent, and his error seems to lie more especially in those for the potassium salts. In some cases he finds the solubilities three or four times greater than my determinations indicate them to be.

		K, Ni.	K, Co.
T.	Parts per liter	162	453
L.	" " "	69	129

It is difficult to account for such discrepancies, even when the fact is taken into consideration that Tobler's work was done long before the newer methods for determining solubilities were known. Another instance of the unreliability of his results is seen in the fact that he obtained a very regular solubility curve for potassium ferrous sulphate, between 0° and 70°, although Küster and Thiel have since shown[2] that at about 30° there is a sharp break, representing the transition:

$$K_2Fe(SO_4)_2.6H_2O \rightleftarrows K_2Fe(SO_4)_2.4H_2O + 2H_2O.$$

In addition to the bivalent metals mentioned above, compounds of this series are also formed by chromium[3] and vanadium,[4] but these are too unstable to permit of accurate deter-

[1] Ann. Chem. (Liebig), **98**, 193.
[2] Ztschr. anorg. Chem., **21**, 116.
[3] Péligot: Ann. chim. phys. [3], **12**, 546.
[4] Piccini: Ztschr. anorg. Chem., **19**, 204.

mination. From the remaining eight bivalent metals, forty salts are theoretically obtainable, and all but two of these, the K—Mn, and K—Cd, compounds have been described. These thirty-eight salts have all been investigated by me, although only the compounds, the solubilities of which are included in the above table, yield data that are suitable for comparison.[1] The caesium salts of all eight metals are easily obtained, although they are far more soluble than those of any other alkali metal. An indication of the much greater readiness of caesium to enter into salts of the series, as compared with potassium, for instance, is seen in the fact noted by Tutton,[2] that while several of the potassium salts are opaque, the caesium compounds of the same metals are almost invariably transparent. This is especially true of the cupric salts. Except in the case of the manganese and cadmium compounds, furthermore, no special precautions are required, with the caesium salts, to prevent the formation of salts with less water of crystallization. The salts with 6 molecules of water result within quite a wide range of temperature.

In the case of potassium, this is true only of the compounds of nickel, cobalt, copper, and zinc. The salts of the other metals form only at low temperatures, and with manganese and cadmium, where the caesium compounds are obtained with difficulty, they do not exist at all. So far as I know, this is the only instance yet noted in which the very marked tendency of caesium to enter into double salts, as compared with potassium, cannot be referred to the fact that the caesium compounds are the less soluble, and it is of particular interest for that reason. In the case of double halides a large number of caesium compounds have been prepared by Wells and others, for which no analogues of potassium can be obtained.[3] But in all such cases, I believe, the caesium salts are very difficultly soluble. The fact that the same phenomena occur when the caesium salts are the more soluble, indicates that a specific tendency for each metal must be taken into considera-

[1] The others are partially decomposed by water, with precipitation of one of their constituent salts.

[2] J. Chem. Soc. 1893, 337.

[3] As an instance may be cited the salt of quadrivalent antimony, Cs_2SbCl_4; Wells and Metzger: This JOURNAL, **26**, 268.

tion, which is not to be confused with ease of isolation, and does not invalue solubility at all. This is more or less inconsistent with the assumption by which the ionic hypothesis explains double salt formation. For, to take an instance which fully satisfies that assumption, the formation of the compound $KAg(CN)_2$ would proceed thus:

$$Ag^+ + CN^- + CN^- = Ag(CN)_2^-.$$

In other words, it should make no difference whether the alkali cyanide solution contains potassium ions or caesium ions, for these take no part in the reaction. Only provided the solubility products of the caesium compounds were lower than those of the potassium salts should there be any difference in the readiness with which they are obtained. We find in the double sulphates a very pronounced difference, however, although the caesium salts are in almost every instance twice as soluble, in gram-molecules, as those of potassium:

	Mg.	Mn.	Fe.	Ni.	Co.	Cu.	Zn.	Cd.
Cs	1.106	1.570	1.967	0.495	0.810	0.882	0.738	2.455
K	1.025	....	....	0.209	0.391	0.350	0.393	....

The solubility of the K,Mg salt here given does not admit of strict comparison with the others, for at 25° the salt is partially decomposed by water, separating a small proportion of its potassium sulphate. An observation to this effect had already been made by Schwarz,[1] and was confirmed by a determination of the ratio of potassium to magnesium in the residue of the saturated solution:

2.752 grams residue gave 1.2921 grams $Mg_2P_2O_7$.

Calculated, 1.0461 " "

Ratio, K : Mg = 2 : 1.49.

No attempts were made to prepare the potassium compounds of manganese and cadmium. The fact of their non-existence seems to have been fully established by Tutton.[2] No reliable determinations, furthermore, could be made on the potassium ferrous salt. That a change of some sort takes place in this compound at 25° is indicated in the fact that after saturation is complete a fine sediment can be seen mixed with the crystals, provided the latter have not been very thor-

[1] Dingler, **198**, 159.
[2] *Loc. cit.*

oughly powdered, and this increases with the length of the digestion. I made no investigation to determine whether this is due to the separation of potassium sulphate or of the salt $K_2Fe(SO_4)_2.4H_2O$, the formation of which, according to Küster and Thiel, should take place at a very slightly higher temperature. In view of the behavior of potassium magnesium sulphate, however, it might readily be expected that the first supposition is true.

In the case of the alums, it was found that the order of solubilities of the compounds of the alkali metals proper was the reverse of that of the atomic weights of the latter. In the present series we not only find the caesium salts more soluble than those of potassium, but the rubidium salts are not intermediate between them. The solubilities of the rubidium salts

Mg.	Mn.	Fe.	Ni.	Co.	Cu.	Zn.	Cd.
0.521	0.857	0.579	0.142	0.220	0.241	0.236	1.615

are in every case well below, instead of higher than those of the corresponding potassium salts. The rubidium compounds can all be obtained within quite wide ranges of temperature, like the caesium salts, and since, in addition to this, they are much more sparingly soluble than the compounds of the other alkali metals, they are the most easily prepared and purified of all the salts examined.

The fact that for the compounds of each bivalent metal, the order in which the alkali metals fall is invariably the same,

$$Rb \rightarrowtail K \rightarrowtail Cs,$$

very clearly indicates the specific influence of the alkali metal upon the solubilities, and shows that the solubilities are not at all dependent upon the atomic weights of the alkali metals. This is further borne out by the behavior of the ammonium and thallium salts. The latter are by far the least soluble of all, although the compounds of caesium, which has the next highest atomic weight, are the most soluble.

	Mg.	Mn.	Fe.	Ni.	Co.	Cu.	Zn.	Cd.
Tl	....	....	....	0.070	....	0.122	0.129	....

As the blanks here indicate, the thallium salts could be obtained only with difficulty, in spite of their low solubility.

The salts resulted with all the bivalent metals, but those the data for which are given are the only ones on which determinations could be made. With the magnesium, manganese, iron, and cadmium compounds the separation of thallium sulphate begins as soon as water is added, and proceeds until all the sulphate of the heavy metal has passed into solution. The cobalt salt is only partially decomposed, even on prolonged digestion. In one experiment with the salt the found solubility was 0.143 gram-molecule, and the residual undissolved salt was mixed with about one-fourth its bulk of thallium sulphate.

The ammonium salts, on the other hand, stand next to caesium in their solubility, although the molecular weight of the complex (NH_4) is lower than the atomic weight of any alkali metal in the series. They are also much more readily formed than the potassium salts, although more soluble, compounds being obtainable with all the bivalent metals. The cupric salt alone is partially decomposed by water.

In view of the fact that the solubilities of the salts, even of the alkali metals proper, do not conform to the atomic weights of the latter in their order, it would obviously be idle to speculate upon the behavior of the compounds of thallium from the standpoint of that metal's position in the periodic system. Neither its position nor its atomic weight can be brought into correlation with these solubilities. The only conclusion which can be drawn without prejudice is that *the effect of each univalent metal upon the solubility of the salts is a specific one, retained throughout all its compounds in the series, and totally independent of its atomic weight.*

The same is true of the bivalent metals. In the second family, for instance, we find the order to be, not

$$Mg \rightarrowtail Zn \rightarrowtail Cd,$$

as in the atomic weights, nor the reverse, but

$$Zn \rightarrowtail Mg \rightarrowtail Cd.$$

	Zn.	Mg.	Cd.
Rb	0.236	0.521	1.615
NH_4	0.480	0.791	2.125
Cs	0.738	1.106	2.455

For the members of the eighth family also, the order is different from that of the atomic weights. The nickel compounds are more sparingly soluble than those of any other bivalent metal in the series, and the cobalt salts stand between these and the ferrous compounds.

	Ni.	Co.	Fe.
Rb	0.142	0.220	0.579
NH_4	0.264	0.391	1.044
Cs	0.495	0.810	1.967

Adjacent to this group is manganese on the one hand, copper on the other. The manganese salts are, in general, less

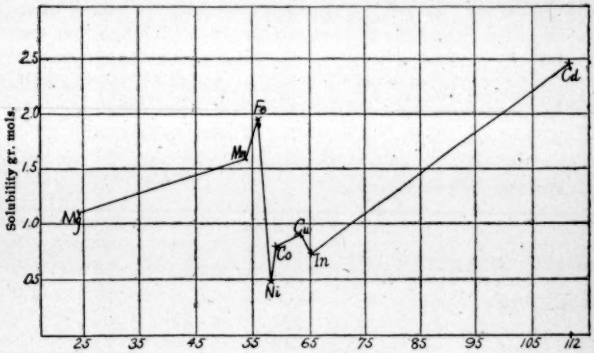


Fig. I.

soluble than those of iron, the cupric compounds more soluble than those of cobalt. For the caesium salts, for instance, we have :

	Mn.	Fe.	Co.	Cu.
Cs	1.570	1.967	0.810	0.882

Obviously, no rule can be laid down by which the solubilities can be explained by the positions of the bivalent metals. Nor can any gradation be observed according to increasing atomic weights of all the elements. The perfect independence of the solubilities from the atomic weights throughout is forcibly shown in Fig. I., where the data for the caesium salts are

plotted with the atomic weights of the bivalent metals as abscissae.

As in the case of the univalent metals, *the influence of the bivalent metal is specific, and independent of its atomic weight and of its position in the system.*

Similar conclusions had previously been reached in the case of the alums. It was there possible to calculate, indirectly, a constant which expressed this specific influence for each metal, that of one metal of the same valence being taken as the standard. Calling the difference between the solubilities of the alums of a given trivalent metal with two alkali metals, the "solubility increment" for the latter (thus, Incr. $Al_{m_2-m_1}$), it was found from the experimental data that the ratio between the corresponding increments for two trivalent metals is approximately the same, no matter which alkali metals m_2 and m_1 represent. The increment ratios,

$$\frac{\text{Incr. } V_{m_2-m_1}}{\text{Incr. } Al_{m_2-m_1}},$$

for instance, are as follows:

Table III.

m_2.	m_1.	Ratio.
NH_4	Cs	3.18
Tl	Cs	3.39
Rb	Cs	3.41
NH_4	Rb	3.15
Tl	Rb	3.35
NH_4	Tl	3.03

The ratios between the increments for aluminium and the remaining trivalent metals are constant to about the same degree. If we adopt aluminium as a standard (the standard will below be denoted as the *initial* metal), these ratios give directly the effect produced by the substitution of the other trivalent metals for aluminium in the salts of the latter. Assuming that the variations in the ratios are due to experimental error, it follows that as soon as the solubilities of two corresponding salts of each trivalent metal are known the others can be calculated. I thought it probable that the same would be true of the salts of the bivalent metals, but found

that in this case there can be no thought of a constant increment ratio. For the series cobalt-nickel (nickel being taken as the initial metal) the following increment ratios were obtained :

Table IV.

m_2.	m_1.	Ratios.
Cs	Rb	1.67
Cs	K	1.46
Cs	NH_4	1.26
NH_4	Rb	2.40
NH_4	K	2.21
K	Rb	2.55

These variations in the increment-ratios are satisfactorily explained, however, if we assume that three solubilities for each bivalent metal must be known, instead of two. It has been found that the relation between the solubilities of corresponding salts of any two bivalent metals is very exactly expressed by the quadratic equation,

$$(1) \quad y' = ay^2 + 2by + c,$$

in which y and y′ are the salts of two bivalent metals with the same univalent metal.

The constants a, b, and c readily admit of chemical interpretation. If y'_1, y_1, y'_2, y_2, and y'_3, y_3 are three solutions of this equation, then,

$$\begin{aligned} y'_1 &= ay_1^2 + 2by_1 + c, \\ y'_2 &= ay_2^2 + 2by_2 + c, \\ y'_3 &= ay_3^2 + 2by_3 + c, \end{aligned}$$

from which, after subtraction, we obtain,

$$(2) \quad \begin{cases} \dfrac{y'_1 - y'_2}{y_1 - y_2} = a(y_1 + y_2) + 2b \\ \dfrac{y'_2 - y'_3}{y_2 - y_3} = a(y_2 + y_3) + 2b \end{cases}$$

Eliminating b, the expression for a becomes,

$$a = \frac{\dfrac{y'_1 - y'_2}{y_1 - y_2} - \dfrac{y'_2 - y'_3}{y_2 - y_3}}{y_1 - y_3}.$$

That is, a is the average rate of change of the increment ratios.

The constant $2b$ is the limit to which the increment ratios approach. In the equation (2) it is given as the increment ratio minus the product of a into the sum of the solubilities of the two salts of the initial bivalent metal. If a is zero, then the increment ratio becomes $2b$, and is, therefore, constant. This was the assumption tacitly made in the mathematical treatment of the solubilities of the alums. The increment ratio approaches more closely to $2b$, furthermore, the less the solubilities of the two salts of the initial element $(y_1 + y_2)$ are, the correction in that case being very small. It is probable, therefore, that in salt series of which the members are very sparingly soluble, the general relation would hold approximately true:

$$\frac{y'_1 - y'_2}{y_1 - y_2} = 2b.$$

If in the equation

$$y' = ay^2 + 2by + c,$$

we set $y = 0$, then $y' = c$, whence it follows that c would be the solubility of a salt of the second bivalent metal when that of the corresponding compound of the initial metal is zero. In the tables given below, the values for c were calculated from the equation

$$c = y'_1 - y_1 \frac{y'_1 - y'_2}{y_1 - y_2} + ay_1y_2.$$

For the derivation of the values of these constants three solubilities must, of course, be known for each bivalent metal, and a fourth is necessary to test their validity. Unfortunately, data can be obtained for four or more salts only in the case of nickel, cobalt, copper, and zinc. With these salts the agreement between the values of each constant, when derived from different solubilities, is remarkable. In the following tables nickel has been retained as the initial bivalent metal throughout, not only because the solubilities of its salts with all the univalent metals could be measured, but because, being the least soluble of all, their determination was the least

subject to experimental error. Under y_1, y_2, y_3, are given the various combinations of salts by which the constants are derived. The values for *c* are expressed in thousandths of gram-molecules per liter. The columns i give the increment ratios as observed, and as calculated from the equations (2), using for *a* and *b* the values marked by asterisks. The observed increment ratios are uncertain by one or two units in the second decimal, and the difference between the observed and calculated values for them are therefore well within the limit of error.

Table V.—Nickel-Cobalt.

y_1.	y_2.	y_3.	*a*.	2*b*.	*c*.	i.	i Observed.
Cs	NH_4	Rb	—0.00320*	3.70	—243	1.27	1.26
Cs	NH_4	K	—0.00325	....	....	....	....
Cs	K	Rb	—0.00313	3.70	—244	1.45	1.46
NH_4	K	Rb	—0.00300	3.72	—247	2.19	2.21
Cs	Rb	..	....	3.70*	—239*	1.66	1.67
NH_4	Rb	..	....	3.70	—240	2.40	2.40
K	Rb	..	....	3.80	—237	2.58	2.55

Table VI.—Nickel-Copper.

y_1.	y_2.	y_3.	*a*.	2*b*.	*c*.	i.	i Observed.
Cs	K	Tl	+0.0005*	1.52	+12	1.87	1.86
Cs	K	Rb	+0.0005	....	....	....	....
K	Rb	Tl	+0.0002	1.51	+14	1.69	1.68
Cs	Rb	Tl	+0.0005	1.51	+16	1.83	1.82
Cs	Tl	..	....	1.52*	+13*	1.80	1.79
K	Tl	..	....	1.50	+15	1.65	1.64
Rb	Tl	..	....	1.54	+13	1.63	1.65

Table VII.—Nickel-Zinc.

y_1.	y_2.	y_3.	*a*.	2*b*.	*c*.	i.	i Observed.
Cs	NH_4	K	—0.0016	2.33	—26	1.12	1.12
Cs	NH_4	Tl	—0.0016*	....	....	....	....
Cs	K	Tl	—0.0016	2.33	—26	1.20	1.20
NH_4	K	Tl	—0.0015	2.34	—25	1.57	1.58
Cs	Tl	..	....	2.33*	—26*	1.43	1.43
NH_4	Tl	..	....	2.33	—26	1.81	1.80
K	Tl	..	....	2.34	—27	1.89	1.90

The most reliable values for the three constants are those marked by asterisks, the increments $y_1 - y_3$ and $y_2 - y_3$ being

there the largest, and consequently the least influenced by experimental error. Adopting these values, we have, as the expression of the relation which the solubilities of the salts of cobalt, copper, and zinc bear to those of nickel, the equations:

$$y_{Co} = 3.70\,y - 0.0032\,y^2 - 0.239;$$
$$y_{Cu} = 1.52\,y + 0.0005\,y^2 + 0.013;$$
$$y_{Zn} = 2.33\,y - 0.0016\,y^2 - 0.026.$$

The value for a, it will be seen, is in each case very small, and in the nickel-copper series, where it is only +0.0005, the increment ratios approach very closely to the value of $2b$ itself.

Since these equations are satisfied by the solubilities of the salts of any alkali metal, all that is necessary to obtain a measure for the influence of any alkali metal upon its compounds is to adopt the nickel salt of one of these as a standard, and substitute for this value of y the product my, where m is the ratio between the solubilities of the standard salt and second salt of nickel. In the form

$$y_{M^{II}} = am^2y^2 + 2bmy + c,$$

then, the general formula would give, by the substitution of corresponding values for the univalent and bivalent metals, respectively, the solubility of any salt in the series. Adopting caesium nickel sulphate as a standard, the values for m are:

	Cs.	NH_4.	K.	Rb.	Tl.
m	1.00	0.533	0.422	0.287	0.141

These constants give the following solubilities in the cobalt, copper, and zinc series. Under D is given the difference from the observed solubilities:

Table VIII.

	Co.	D.	Cu.	D.	Zn.	D.
Tl	....	....	0.122	0.000	0.130	+0.001
Rb	0.222	+0.002	0.239	−0.002	0.270	+0.034
K	0.394	+0.003	0.352	+0.002	0.392	−0.001
NH_4	0.515	+0.002	....	....	0.478	−0.002
Cs	0.808	−0.002	0.887	+0.005	0.738	0.000

There is but one instance, that of the zinc-rubidium salt, in

which the error exceeds that of experimental error. In the other cases of abnormal solubility noted in the course of the work, it has been possible to trace the difference to more or less complete decomposition by water, with separation of one of the constituent salts; but for the error in this case I am unable to account. Its magnitude is not very great, however, and in view of the remarkable coincidence between calculated and observed results throughout the rest of the table, may, for the time being, be disregarded. I hope later to make a special examination of the various zinc salts, with the object of ascertaining its cause. The validity of the relation between the solubility of the salts in general is emphatically shown by the fact that I was able to prophesy the solubilities of some of the compounds in the series within the limit of error, before they had been made at all.

Of course, the above general equation would give the solubility of a salt of zinc, etc., for any value of y whatsoever, without regard to whether the corresponding nickel compound actually exists or not. The possible values for y, however, are limited by a strange rule, which must, for the time being, be regarded as purely empirical, as it does not hold in the case of the alums. The solubilities of the salts of any given bivalent metal satisfy the equation

$$M_{II}\frac{Cs-m_1^I}{Cs-m_2^I}=n^e,$$

where n is a constant, and the exponent e is 1, 2, or 3, according to how far removed from one another the salts of the metals M_1^I and M_2^I are in the order of solubilities

$$Cs \rightarrowtail NH_4 \rightarrowtail K \rightarrowtail Rb \rightarrowtail Tl.$$

The accuracy of the rule is shown by the ratios given in

Table IX.

	e.	Ni.	Co.	Cu.	Zn.
$\frac{Cs-NH_4}{CS-K}$	1	0.81	0.71	....	0.75
$\frac{Cs-K}{Cs-Rb}$	1	0.81	0.70	0.83	0.70

	c.	Ni.	Co.	Cu.	Zn.
$\frac{Cs—Rb}{Cs—Tl}$	1	0.83	....	0.84	0.82[1]
$\frac{Cs—NH_4}{Cs—Rb}$	2	0.81	0.71	....	0.72
$\frac{Cs—NH_4}{Cs—Tl}$	3	0.81	....	....	0.75
$\frac{Cs—K}{Cs—Tl}$	2	0.82	....	0.84	0.75

The agreement between the calculated and observed increment ratios for the different bivalent metals, as given in Tables V. to VII., is very much more exact than that found in the case of the alums, Table IV., when the ratio was assumed to be constant. This led me to test the solubilities of the alums by the above quadratic equation. In my previous article, as has been stated, the tacit assumption had been made that a here equals zero, in which case the increment ratio is constant, and equals $2b$. It was found that a somewhat more exact expression for the solubilities in this series as well, was obtained by the new formula, although a is in fact much smaller in each case than for the double sulphates of any of the bivalent metals except copper. It will suffice here to give the values for a, b, and c for a single one of the alum series. In that of aluminium-vanadium, aluminium being taken as the initial trivalent metal, these values are as follows :

Table X.—Aluminium-Vanadium.

y_1.	y_2.	y_3.	*a.*	$2b$.	*c.*	i.	Observed.
NH_4	Tl	Rb	—0.0009	3.54	—26	3.03	3.03
NH_4	Tl	Cs	—0.0009*	....	....	....	....
NH_4	Rb	Cs	—0.0008	3.55	—29	3.14	3.15
Tl	Rb	Cs	—0.0007	3.56	—29	3.33	3.35
NH_4	Cs	..	....	3.54*	—25*	3.18	3.18
Tl	Cs	..	....	3.52	—29	3.37	3.39
Rb	Cs	..	....	3.47	—25	3.47	3.41

[1] The variations here are due to the slightly abnormal solubility of the zinc-rubidium salt. Using for the latter the calculated solubility (Table VIII.) the ratios into which this salt enters are

$$\frac{Cs—K}{Cs—Rb} = 0.74, \quad \frac{Cs—Rb}{Cs—Tl} = 0.75, \quad \frac{Cs—NH_4}{Cs—Rb} = (0.74)^2,$$

in close agreement with the ratios for the other salts.

Using the equation

$$y_v = 3.54\ y - 0.0009\ y^2 - 0.025,$$

the calculated solubilities for the vanadium alums are as follows:

	Cs.	Rb.	Tl.	NH_4.
	0.020	0.180	0.573	1.211
D =	0.000	+0.003	0.000	+0.001

For the aluminium-chromium and aluminium-ferric series, similarly, the equations

$$y_{Cr} = 1.37\ y - 0.0008\ y^2 - 0.002$$
$$y_{Fe} = 4.84\ y - 0.0013\ y^2 - 0.019$$

form a much more exact expression for the solubilities of the chromium and ferric alums than did that previously derived.

The relations discussed above indicate very conclusively that *in a group of isomorphous compounds the effect of a given element upon the solubility of its compounds in the series is constant throughout all these compounds.* The general formula for its calculation is the same for the salts of both bivalent and trivalent metals, and in all probability, therefore, we have before us the working, in two instances, of a general law, which, after development in other series, may be of very great importance in the systematization of inorganic compounds.

The general applicability of an equation of the form

$$y' = ay^2 + 2by + c$$

shows that if the solubilities be plotted with the salts of the initial element as ordinates, and those of the second metal as abscissae, a parabola always results. Fig. II. gives its form for the aluminium-vanadium series among the alums, and for the nickel-cobalt, nickel-copper, and nickel-zinc series in the other group. It will be seen that in the aluminium-vanadium and nickel-copper series, where the values of a are extremely small (−0.0009 and +0.0005, respectively), the parabolas very nearly approach to being straight lines.

This method of presentation is of peculiar interest, because in it no account whatsoever is taken of the atomic weights. The latter do not even enter into the values of a and b, which

Salts of nickel
Salts of aluminum
Salts of bivalent metals.
Salts of vanadium
Ni-Zn
Ni-Cu
Ni-Co
Al-V

FIG. II.

determine the form of the parabolas, and are calculated merely from the increment ratios. The repeated crossings of the curves for the different bivalent metals, furthermore, show that there is no correlation between solubilities and atomic weights, except in the fact that the former are expressed in gram-molecules. For certain reasons which will appear later, however, it is better to adhere to the more conventional means of presentation, using the solubilities as ordinates and atomic weights as abscissae.

This was the method employed in my articles on the alums, in which, for abscissae, the atomic weights of the trivalent metals were chosen. If a were zero, the lines connecting the solubility-points of the alums of two trivalent metals with the same univalent metal, as in Fig. I., would then have a common point of intersection. This assumption was made the basis of my calculations in that paper. When a is too large to be neglected, however, these lines, as will be shown, instead of meeting in a point, are tangential to a hyperbola, one of the asymptotes of which is the perpendicular erected at the x-value for the initial element.

If the atomic weight of nickel be represented by σ, and that of a second bivalent metal by $\sigma + h$, and the solubilities of the salts of the two with a given univalent metal be y and y′, respectively, then the equation of the line joining y and y′ will be :

$$(3)\quad \frac{Y-y}{X-\sigma} = \frac{y'-y}{h}.$$

Taking two new corresponding solubilities, $y + \Delta y$, and $y' + \Delta y'$, we find for the point of intersection of the line (3) with that joining the new points,

$$(4)\quad \begin{aligned} X &= \sigma + \frac{h}{1 - \frac{\Delta y'}{\Delta y}} \\ Y &= \frac{y' - y\,\frac{\Delta y'}{\Delta y}}{1 - \frac{\Delta y'}{\Delta y}}. \end{aligned}$$

Since the equation

$$(5)\quad y' = ay^2 + 2by + c$$

is also satisfied by $y + \Delta y$, $y' + \Delta y'$,

$$(6)\quad y' + \Delta y' = a(y + \Delta y)^2 + 2b(y + \Delta y) + c.$$

After subtracting (5), therefore,

$$(7)\quad \frac{\Delta y'}{\Delta y} = 2ay + 2b + a\Delta y.$$

Now let the two lines in question approach coincidence. As Δy approaches zero, from (7), $\frac{\Delta y'}{\Delta y}$ becomes $2ay + 2b$. Substituting this value in (4), the point (X, Y),

$$(8)\quad \begin{aligned} X &= \sigma + \frac{h}{1 - 2(ay + b)} \\ Y &= -\frac{ay^2 - c}{1 - 2(ay + b)} \end{aligned},$$

becomes the point of contact of the line joining (σ, y), $(\sigma + h, y')$ with the curve touched by *all* lines joining corresponding values of y and y', or corresponding solubility-points. The equation of this curve, which is an hyperbola, may be found by eliminating y in (8). This gives

$$(9)\quad K^2(x - \sigma)^2 + 4ah(X - \sigma)Y - 2h(1 - 2b)(X - \sigma) + h^2 = 0,$$

where

$$K^2 = (1 - 2b)^2 - 4ac.$$

The center is the point $\left(\sigma, \frac{1 - 2b}{4a}\right)$ and the asymptotes are:

$$x = \sigma, \quad K^2(x - \sigma) + 4ahY - 2h(1 - 2b) = 0.$$

The tangents parallel to the x-axis touch at the points:

$$\left(\sigma \mp \frac{h}{k}, \quad \frac{1 - 2b}{2a} \pm \frac{K}{2a}\right),$$

and from these data the curve may be located, and by (8), as many points located thereon as we wish.

In the cases before us, the hyperbolas are all very thin. A peculiar fact, in the series nickel-cobalt and nickel-zinc, is

that the lines connecting the caesium salts are tangential to one branch of the curve, those for the remaining salts to the other. In both these series the upper branch lies to the right of the nickel perpendicular. In the nickel-copper series, on the other hand, the upper branch lies to the left, and all the lines are tangential to this. This case is represented in Fig. III.

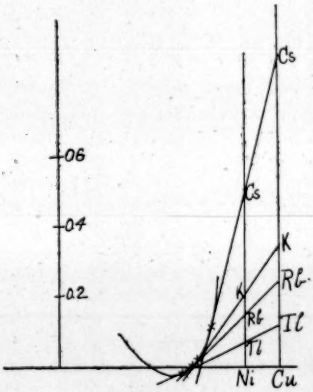


Fig. III.

A consideration of this figure brings out one very important point, not shown by the first and simpler method of plotting, and for the purpose of illustrating which, therefore, this method has been retained. In the nickel-copper series all the lines are tangent to the curve at points lying on the same side of that at which it is touched by the horizontal tangent, and the curve lies outside the two perpendiculars. All these lines are, therefore, inclined upward, and the solubility of each cupric salt, accordingly, is greater than that of the corresponding nickel compound. This, however, is by no means necessarily the case. If the hyperbola, or that part of it included between the points of tangency, lay between the two perpendiculars, then (Fig. IV.) if the successive solubilities of the salts of the initial element ran A $\mapsto$ B $\mapsto$ C, those of the second

would lie in the order $C_1 \mapsto B_1 \mapsto A_1$. The order of solubility would be reversed throughout. The most soluble compounds

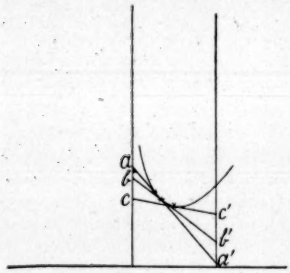


Fig. IV.

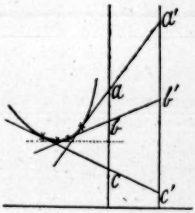


Fig. V.

for the initial element would be the least soluble for the second. This is the most complicated case, and has not yet, with certainty, been observed.

With the hyperbola lying outside the perpendiculars, secondly, let us assume its position to be such that the y-value of the horizontal tangent is intermediate between the extremes of solubility for the compounds of the initial element. *Then (Fig. V.), for all points lying below the horizontal the solubilities for the second element will be less than for the first, and for those above it they will be greater.* In the figure we have $A < A_1$, $B < B_1$, but $C > C_1$. Two instances are shown by the compounds of the bivalent metals in which this interesting relation occurs: in both, the extreme solubilities for the initial element are in the one case less, in the other case greater, than those for the second. In the zinc-copper series we find:

Zn–Tl	0.129	$>$	Cu–Tl	0.122;
Zn–Cs	0.738	$<$	Cu–Cs	0.882.

In the zinc-cobalt series:

Zn–Rb	0.236	$>$	Co–Rb	0.220;
Zn–Cs	0.738	$<$	Co–Cs	0.810.

Examined alone, these figures apparently stand at utter variance to one another, and seem to forbid all possibility of our

ever measuring the influence of an element upon its compounds in properties which are not strictly additive. It is probably due largely to such apparent contradictions, of which the literature is full, that so little work has been done toward the exact systematization of inorganic chemistry. But these solubilities represent merely certain points in a general scheme. Taken alone, no theoretical importance can be attached to them as a measure of the influence of zinc or cobalt upon their compounds, for to judge by the caesium salts would be to disregard the opposite relation of the rubidium compounds. As soon as more solubility-points for the two bivalent metals have been determined, however, these inconsistent data are explained, and we obtain from the solubility increments an equation which gives the solubilities not only of the caesium and rubidium salts, but of all.

The lack of any relation between the solubilities and the positions of the elements in the periodic system, or their atomic weights, renders the behavior of the ammonium salts important, for if atomic weight is not the determining cause of the varying solubilities, then there is no need of distinguishing the compounds of a complex radical from those of elements pure and simple, in any reactions which do not involve the decomposition of the radical itself. The ammonium salts follow exactly the same law as do the salts of the alkali metals, and in any exact and complete system of classification, therefore, they are as much entitled to a place as the metallic salts. The correct basis for classification, then, cannot be the atomic weights, for ammonium has no atomic weight. The periodic system ignores all resemblance between ammonium compounds and those of the alkali metals. For the purpose of rough, temporary classification this is all very well. It is sufficient to regard the ammonium salts as "imitating" the metals. But if we wish to make our system a guide toward ascertaining what the actual determining cause of the properties of inorganic compounds is, we must seek one which will include complex radicals, and which, incidentally, will differentiate between the compounds of an element in different degrees of oxidation.

Such a system is to-day impossible, for we know with ex-

actitude almost nothing concerning gradation in the properties of inorganic compounds. But if the influence of an element upon its compounds of a series is constant throughout, as from the above work appears to be the case in the matter of solubility, then the thought of an exact system is not very visionary. To attain it, however, analogous compounds must be given consistent comparative study, and quantitative data be obtained concerning them. In each series of compounds studied, furthermore, it is of prime importance to include as many representatives of the variable elements or groups as possible. The relative solubilities of the thallium and caesium double sulphates of zinc and copper, and of the rubidium and caesium salts of zinc and cobalt, show that no definite information can be gained of the influence of an element upon its compounds until at least three salts of each metal have been examined. A fourth or a fifth must be examined to prove the validity of the deductions drawn on the basis of the data thus obtained. To-day, so far as I can ascertain, there is not a single instance in the inorganic literature, where a property like solubility has been accurately determined for the fourth salt in such a series. There are almost no cases, where comparable and reliable data for three are at hand. The most essential features of the periodic system have hardly ever been tested by quantitative measurements.

The conclusions drawn in this paper regarding the independence of the solubilities from the atomic weights is open to criticism upon one point, which arises in this connection. To ascertain the influence of a given bivalent metal upon the double sulphate, we must know the solubility of at least three salts of both this and the initial metal. But the data thus derived are in a measure comparable with those which would be obtained from a consideration of the salts with a single alkali metal, for in the $SO_4^{=}$ group we are adhering to one representative of another variable constituent. It is barely possible that after a similar examination of the corresponding selenates, a combination of the constants obtained in the two series, which would thus give the influence of the metal upon any of its compounds in the series $M_2^{I}M^{II}(RO_4)_2.6H_2O$, would bring the metals into the order of their atomic weights.

Unfortunately, except in the one compound,

$$(NH_4)_3Mg(CrO_4)_2.6H_2O,$$[1]

R is represented only by sulphur and selenium, and for accurate comparison three substituent elements are necessary. Two much more suitable series for the investigation of this point would be the salts of the general formulas $M^{I}_{2}M^{IV}X_6$ and $M^{II}M^{IV}X_6.6H_2O$, in which all three symbols have several representatives. The second formula should theoretically be conformed to by 192 different salts. These two series I should like to reserve to myself for future study.

My thanks are due to Professor Percy F. Smith, of the Sheffield Scientific School, for many suggestions embodied in the mathematical part of the above work.

NEW HAVEN, April 2, 1902.

THE INACTIVITY OF LIPASE TOWARDS THE SALTS OF CERTAIN ACID ETHERS CONSIDERED IN THE LIGHT OF THE THEORY OF ELECTROLYTIC DISSOCIATION.

BY J. H. KASTLE.

While studying the kinetics of lipolytic hydrolysis, a subject that has been under investigation in this laboratory now for some time, it was thought desirable to try the effect of varying amounts of water on the hydrolysis of ethereal salts by lipase. In order to accomplish this satisfactorily it was found necessary to employ a very soluble ethereal salt and one which the ferment could readily hydrolyze. On account of the solubility of certain salts of some of the acid ethers it seemed probable that these substances might be employed to advantage in the investigation of this particular phase of the problem. Such a substance is sodium ethyl succinate. The fact that diethyl succinate is readily hydrolyzed by lipase furnished an additional reason for using sodium ethyl succinate in the preliminary experiments. While this salt was never obtained in as satisfactory a condition of purity as could be desired, it was observed that lipase could not effect its

[1] Grailich, A. W., 27, 175. The potassium compound crystallizes with $2H_2O$.

hydrolysis. This seemed the more remarkable in view of the ease with which the diethyl succinate is hydrolyzed by the lipolytic ferment.

In view of this somewhat remarkable and interesting result it seemed advisable to test the conduct of lipase towards the salts of other acid ethers, and also, by way of comparison, its action on the corresponding neutral ethers.[1] Up to the present the action of the ferment on the mono- and diethyl ethers of eight dibasic acids has been studied. The following results were obtained:

Fumarates.—Diethyl fumarate is very readily hydrolyzed by lipase. This has been demonstrated by numerous experiments. On sodium ethyl fumarate, on the other hand, lipase is without action in twenty-four hours, at 40° C.

Oxalates.—Diethyl oxalate is so easily hydrolyzed, even by pure water, that it was found difficult to determine whether lipase accelerated the hydrolysis. By working at 0° C., however, it was observed that the active ferment accelerates the hydrolysis.

On potassium ethyl oxalate lipase has no action, or, if any, it retards the hydrolysis. Tubes containing small amounts of this salt and strong unfiltered hepatic extracts, and the boiled controls showed no difference in acidity in twenty-four hours at 40° C. On the other hand, with clear, weaker solutions of hepatic lipase and this salt, the boiled controls showed a slight acidity after twenty-four hours at 40° C., whereas the tubes containing the active ferment remained neutral.

Phthalates.—Diethyl phthalate is slowly hydrolyzed by lipase. This has been proved in numerous experiments. On the other hand, it is not acted on by pure water at ordinary temperatures or at 40° C. in twenty-four hours.

[1] In testing the conduct of lipase towards the various ethers employed in this investigation the following mode of procedure was generally adopted. Tubes were prepared containing 5 cc. of the active and boiled enzyme. To these litmus was added, together with small amounts of the ether to be tested and a small quantity of toluene as antiseptic. The tubes were then kept at the proper temperature, for the desired interval, any hydrolysis being indicated by the change in color of the litmus. The activity of all lipase extracts and solutions employed in the investigation was repeatedly determined by means of ethyl butyrate during the progress of the work. The solutions and extracts employed were found to hydrolyze 0.0058 to 0.0290 gram of ethyl butyrate in fifteen minutes at 40° C., when 5 cc. of the solution or extract were allowed to act on 0.2300 gram of the ethereal salt.

Barium ethyl phthalate is not hydrolyzed by lipase at ordinary temperature or at 40° C. in twenty-four hours. That such is the case has been demonstrated both with clear and unfiltered extracts of the ferment acting under a variety of conditions. Similar results have been obtained with potassium ethyl phthalate.

p-Nitrosulphobenzoates.—Like most, if not all, of the sulphonic ethers, diethyl *p*-nitrosulphobenzoate is slowly hydrolyzed by pure water. Apparently, lipase does not accelerate the hydrolysis of this ether. In fact, it has been found that clear, dilute solutions of lipase seem rather to retard the hydrolysis than otherwise. On the other hand, with more active unfiltered pancreatic and hepatic extracts the diethyl ether showed no hydrolysis in twenty-four hours at 38° C.

It has also been shown that neither the barium ethyl *p*-nitrosulphobenzoate nor the potassium salt were hydrolyzed by any of the lipase extracts in twenty-four hours at 38° C.

p-Sulphobenzoates.—The monoethyl ether of *p*-sulphobenzoic acid was prepared by passing hydrochloric acid gas into a solution of the acid in absolute alcohol. The excess of alcohol, together with the hydrochloric acid, was evaporated off on the water-bath, the residual syrup diluted with a considerable quantity of water, and neutralized with barium carbonate. The excess of barium carbonate was then filtered off and the filtrate evaporated to crystallization. Barium ethyl *p*-sulphobenzoate was thus obtained in the form of beautiful, thin, white plates. On analysis the salt gave numbers agreeing with the theory for

$$p\text{-}\left(C_6H_4\begin{matrix}COOC_2H_5\\SO_2O\end{matrix}\right)_2Ba + 1\tfrac{1}{2}H_2O.$$

This salt was found to be unacted on by lipase.

The conduct of diethyl *p*-sulphobenzoate has not been determined.

Sulphates.—During the last two years a great many attempts have been made in this laboratory to effect the hydrolysis of barium and potassium ethyl sulphate by means of lipase. All these have resulted in failure. The ferment has

always been found to be inactive towards these salts. The conduct of the ferment towards diethyl sulphate has not been tested.

From these observations one might get the impression that possibly the salts of these various acid ethers are toxic to lipase and that they thereby prevented its action. That such, however, is not the case has been proved by adding small amounts of ethyl butyrate to the contents of the tubes before the conclusion of the tests. In every instance the tubes containing the active ferment showed a marked hydrolysis in a few minutes after the addition of the butyrate, whereas the control experiments gave no evidence of any hydrolysis. In this way it was shown that even after remaining in contact with the salts of these acid ethers for twenty-four hours, or even longer, the ferment was capable of hydrolyzing ethyl butyrate.[1]

This would seem to indicate that the failure on the part of the lipolytic ferment to hydrolyze the salts of acid ethers cannot be ascribed to the toxicity of these substances, but must be due to some other cause. Apparently, the explanation of the difference in the conduct of lipase towards the neutral and acid ethers is to be looked for not in any specific effect which either of these substances may exert toward the ferment, but rather in some fundamental chemical difference in the nature of the two classes of ethereal salts. In this peculiar conduct on the part of lipase we are reminded, at least to some extent, of the remarkable behavior of glucose and emulsine towards α- and β-methyl glucoside. In order to account for the remarkable difference in the conduct of the two ferments to these compounds it has been found necessary to refer it to a corresponding difference in the stereo-configuration of the two glucosides; so in the same way it would seem logical to assume that the difference observed in the conduct of lipase towards neutral ethers and the salts of acid ethers is due in all

[1] It is not intended to convey by this that the salts of the acid ethers are altogether non-toxic to lipase. Like all salts, even including such substances as sodium and potassium chlorides, they have been observed to be somewhat toxic in their effect upon the ferment; but in no case has there been an entire loss of lipolytic activity on the part of any solution of lipase employed in these experiments, as the result of the poisonous action of the substance being tested.

probability to some inherent chemical difference in the nature of these two classes of compounds.

In the light of our present conceptions the most characteristic difference between the diethyl ether of a dibasic acid and a metallic salt of the monoethyl ether of the same acid, so far as their chemical conduct is concerned, is that in aqueous solution the latter is ionized whereas the former is not. This difference is quite as fundamental as a structural one. Might it not account, therefore, for the difference in their conduct towards lipase?

In view of this it became a matter of interest to test the conduct of lipase towards certain derivatives of the monoethyl ethers that are chemically indifferent. Accordingly, ethyl oxamate and ethyl *p*-sulphaminebenzoate were prepared and their conduct towards lipase tested in the usual manner. Both of them were found to be hydrolyzable by the action of the ferment. Briefly, then, the facts as they are known to us at present are these:

First, lipase has been found to hydrolyze a large number of neutral ethers. Among those whose conduct towards the ferment has been tested in this laboratory may be mentioned the following: Ethyl formate, ethyl acetate, ethyl butyrate, ethyl propionate, ethyl isobutyrate, ethyl benzoate, methyl butyrate, amyl acetate, amyl butyrate, diethyl succinate, diethyl oxalate, diethyl fumarate, diethyl tartrate, diethyl phthalate, etc.

Secondly, lipase has been found to be inactive towards the salts of acid ethers, the following having been tested with the ferment: Sodium ethyl succinate, potassium ethyl oxalate, barium ethyl sulphate, potassium ethyl sulphate, barium ethyl phthalate, potassium ethyl phthalate, barium ethyl *p*-sulphobenzoate, sodium ethyl fumarate, barium ethyl *p*-nitrosulphobenzoate, potassium ethyl *p*-nitrosulphobenzoate. Not one of these compounds was hydrolyzed by the ferment.

Thirdly, lipase has been found capable of hydrolyzing chemically indifferent derivatives of certain of the monoethyl ethers, such as ethyl oxamate and ethyl *p*-sulphaminebenzoate.

In the light of these results one is naturally led to connect the inactivity on the part of lipase towards the salts of acid ethers with the electrolytic dissociation of these substances in aqueous solution; and upon the assumption that the hydrolysis of a substance by means of a ferment is always preceded by the combination of the hydrolyte and the enzyme, the results above described may be construed to mean that lipase cannot form combinations with ions but only with molecules. It is interesting to note in this connection that by far the greater number of substances capable of being hydrolyzed by enzymes are, from the standpoint of the theory of electrolytic dissociation, indifferent or non-ionizable substances. These substances are so well known that they do not require mention in this connection. Only a few substances of salt type can be hydrolyzed by ferments. Such substances are potassium myronate and ammonium hippurate. To what extent these substances are ionized in aqueous solution is at present unknown to the writer if, indeed, it has ever been determined.

In view of the very thorough and exhaustive treatment which the whole subject of electrolytic dissociation has received in recent years, it would seem at first sight that quite a number of methods were available for further testing the correctness of these assumptions. Unfortunately, however, such is not the case, for, as frequently happens in investigations of this kind, the instability of the enzyme and its extreme sensitiveness to its chemical environment simply make it impossible to impose conditions which ordinarily are simple enough. Enough has already been done to make it apparent that a great many practical difficulties will have to be overcome before any additional evidence either for or against the views herein advanced is to be obtained. As soon, therefore, as the opportunity presents itself I hope to make a thorough and exhaustive study of the questions suggested by these observations.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, April, 1902.

REPORTS.

Recent Work on the Derivatives of Alkali and Alkaline Earth Metals.

Within the last few years the *Comptes Rendus* has contained a number of brief articles by Moissan and his co-workers on this subject. The only long article was that published by Moissan[1] two years ago, in which he sums up his remarkable work on calcium and its derivatives. A brief report of this article was given in this JOURNAL.[2] A résumé of the many short articles seems timely. The subjects may be classed as follows: Metals, Nitrides, Derivatives of Ammonia and of Ammonium, and Hydrides.

Metals.

Beryllium.—Lebeau,[3] in 1898, obtained pure beryllium by electrolysis of beryllium-sodium fluoride, in a nickel crucible with positive graphite electrodes, the crucible acting as negative electrode. The metal was deposited as a network of crystals, which, after thorough washing with water, form a crystalline powder of white metallic luster. The metal proved to be pure. Previous attempts to prepare beryllium had been either by action of potassium or sodium on beryllium salts, or by electrolysis of the chloride or fluoride, this last method not succeeding because these salts do not conduct the current.

Barium.—Guntz,[4] working at Nancy, says that thus far no barium has been made which was proved pure by analysis. He adopts Maquenne's[5] method of starting from an amalgam containing 3 per cent barium, which is readily obtained by electrolysis of a saturated solution of barium chloride, using mercury as cathode and a platinum-iridium anode, and distilling the amalgam in a vacuum. Hitherto, barium free of mercury has not been obtained in this way, and Guntz owes his success to his method of heating. The porcelain tube was fitted into a tube of refractory earth. Platinum wire was wound about the refractory tube, protected from silica by a brasque of aluminium oxide and magnesium oxide. The whole was covered by several layers of asbestos and an electric current passed through the wire; he could thus obtain, in a porcelain tube of 5 cm. diameter and 30 cm. length, a temperature of 1200° to 1300°, by a current of 600 to 700 Watts. Heating the tube, which contains the amalgam, very slowly, he finds that at 600° mercury

[1] Ann. chim. phys., [7], **18**, 289.
[2] This JOURNAL, **24**, 96.
[3] Compt. rend., **126**, 744.
[4] *Ibid.*, **133**, 872.
[5] Bull. soc. chim. (Paris), **7**, 386.

escapes quietly, leaving a fused amalgam in the boat. At 1000° all mercury has escaped. A higher heat volatilized the barium. It adheres to the iron boat, and in removing it with a chisel it was somewhat oxidized, as his analysis showed. Mercury and barium hydroxide were absent. Pure barium is silver-white and soft as lead; it decomposes water and absolute alcohol. The yellow color ascribed to the alkaline earth metals by earlier observers is caused by presence of nitride.

Strontium.—Henri Gautier,[1] working in Moissan's laboratory, obtains by the action of zinc and of cadmium on strontium iodide, a zinc alloy containing 18 per cent strontium and a cadmium alloy containing 45 per cent cadmium. By heating this last alloy in a current of hydrogen at red heat he obtains strontium hydride.

Guntz,[2] in consequence of Gautier's publication, describes his incomplete work on strontium. He obtains strontium from its amalgam by the method which he used for barium, but has not yet succeeded in getting it quite free of mercury.

Nitrides.

The nitrides of barium and strontium were first isolated by the action of nitrogen on heated impure barium and strontium, and studied by Maquenne.[3] While his specimens were not quite pure, he established their chief properties and their composition, Ba_3N_2 and Sr_3N_2. The calcium nitride is described fully by Moissan[4] in his treatise on calcium. Lithium nitride was first made from impure lithium by Ouvrard[5] and its general properties noted. It may be said of the nitrides of all of these four metals that they are bronze-colored solids that burn in air, are readily acted on by chlorine, phosphorus, sulphur, and notably by water, which decomposes them quantitatively into ammonia and metal hydroxide, and by dilute acids, which give salts of the metal and ammonium.

Guntz[6] made pure lithium nitride from pure lithium, by heating it in a current of nitrogen. He confirms the composition Li_3N given by Ouvrard. He says that when heated in hydrogen the following reaction takes place:

$$Li_3N + 3H_2 = 3LiH + NH_3,$$

while if the hydride of lithium is heated in nitrogen this reaction is reversed:

$$3LiH + N_2 = Li_3N + NH_3.$$

Moissan shows that this is not true of the calcium compounds,

[1] Compt. rend., **133**, 1005.
[2] *Ibid.*, **133**, 1209.
[3] Ann. chim. phys., [6], **29**, 215.
[4] *Ibid.*, [7], **18**, 289; This JOURNAL, **24**, 1.
[5] Compt. rend., **114**, 120.
[6] *Ibid.*, **123**, 995.

for calcium nitride, Ca_3N_2, heated to a red heat, yields hydride, while the reverse does not occur when the hydride is heated in nitrogen.

Metal-Ammoniums.

The fact that potassium and sodium are soluble in liquid ammonia forming blue solutions has been noticed by many chemists. Joannis was the first to make a careful study of the subject, and many articles by him are in the *Comptes Rendus* in the volumes between 109 and 117, inclusive. The date of these articles is too early to include them in this report, but it may be said that Joannis believed in the formation of unstable compounds of the composition KNH_3 and $NaNH_3$, while Seeley and other observers thought the so-called sod-ammonium and potass-ammonium to be merely solutions of the metals in liquid ammonia.

Moissan[1] has settled this question and shown that Joannis was right. To determine the temperature limit at which the substances could form, and whether, indeed, the metals would act on gaseous ammonia, he brought the metals potassium, sodium, lithium, and calcium into contact with a current of dry ammonia gas at a temperature of 100° and at atmospheric pressure. By gradually lowering the temperature he could observe the point at which the ammonia gas attacked the metals. He found that in all cases a compound was formed. The results were:

Dry ammonia gas combines with lithium at +70° with liquefaction.

Dry ammonia gas combines with calcium at +20° without liquefaction.

Dry ammonia gas combines with potassium at —20° with liquefaction.

Dry ammonia gas combines with sodium at —20° with liquefaction.

At any temperature above these the compounds break down into metal and ammonia. If the liquid compounds are kept for a time at these temperatures the excess of ammonia escapes, and the solids KNH_3, $NaNH_3$, and $LiNH_3$ remain. These, as well as the solid calcium-ammonium, $Ca(NH_3)_4$, are stable at temperatures below those given. He modified his experiments and proved that solid ammonia at —80° does not act on any of these metals, but as soon as the temperature rises to the liquefaction-point of ammonia, —75°, the metals are attacked and all except calcium dissolve.

Common Properties of the Metal Ammoniums.—All four excepting calcium give dark-blue solutions in an excess of liquid

[1] Compt. rend., **127**, 685.

ammonia. When this excess is evaporated, bronze-colored solids remain. If any of the four metal-ammoniums are allowed to stand either in solid form or dissolved in liquid ammonia at temperatures somewhat below their decomposition temperatures, they give off hydrogen and form the metal amide

$$LiNH_4 = LiNH_2 + H.$$

The amides of the metals are transparent crystalline substances, little soluble in liquid ammonia. The solid metal-ammoniums are all decomposed by water and take fire in the air. Further properties of this class of compounds have only been published in the articles by Joannis. Moissan promises an exhaustive article on the whole field. As to the valence of calcium in $Ca(NH_4)_4$, Moissan says: "it may be regarded as tetravalent, or it may be that calcium-ammonium is $Ca(NH_4)_2 + 2NH_4$." He inclines decidedly to the former view, thinking that the behavior of the substance does not warrant the latter.

Barium-Ammonium.—Guntz[1] says that barium dissolves in liquid ammonia, forming a bronze-colored liquid.

Strontium-Ammonium.—Guntz[2] says that strontium does not form this compound as readily as barium; at least liquid ammonia does not change color in contact with strontium.

Ammonium Amalgam.—Moissan[3] reviews the history of ammonium amalgam, and decides to determine the exact volumes of ammonia and of hydrogen given off in the decomposition. On account of the solubility of ammonia in water, he deemed it necessary to avoid its use, and used liquid ammonia as solvent. He first proved that sodium amalgam is not attacked by liquid ammonia at temperatures below —35°. On adding dry ammonium iodide the reaction $NH_4I + NaHg_n = NaI + NH_4Hg_n$ takes place without escape of gas, the new amalgam being more fluid. After thorough shaking, washing, and decanting with liquid ammonia to remove sodium and ammonium iodides, the amalgam is cooled to —80°, becoming very hard. After washing with ether saturated with a hydrogen at —80°, the metal is placed in a glass tube with ground-glass stopper and connected with a mercury pump. The tube is exhausted at —80° and the temperature allowed to rise slowly. At —40° the mass begins to liquefy, at —30° swells, and at +15° almost fills the tube, occupying thirty times its original volume. During this decomposition, heat is

[1] Compt. rend., **133**, 872.
[2] *Ibid.*, **133**, 1209.
[3] *Ibid.*, **133**, 803.

set free. Seven concordant analyses of the gas set free showed it to consist of two volumes of ammonia and one of hydrogen. From this work it would appear that the radical ammonium NH_4 or $(NH_4)_n$ exists in the metallic mass prepared below —35°. Moissan, however, does not believe this to be true, but thinks that a metallic hydride of ammonia is formed, which, by decomposition, causes the escape of gas.[1]

Moissan[2] has shown that when sulphur dissolves in liquid ammonia forming a dark-red liquid, this liquid contains a compound of the composition $(NH_3)_2S$, sulph-ammonium, an analogue of the metal-ammonium, which is completely dissociated at ordinary temperature and pressure. It sulphurizes in the cold a large number of elements and compounds, and it forms addition-products with ammonia.

Moissan[3] shows that lithium dissolves in methylamine forming a dark-blue solution, from which, at ordinary temperatures, ammonia escapes, till a bronze-colored solid, $LiNH_2CH_3$, remains, which is stable at ordinary temperature.

Attempts to isolate the Ammonium Radical.—Moissan has attacked this problem in different ways. In one artiticle,[4] referring to the work of O. Ruff[5] on the electrolysis of ammonium iodide in solution in liquid ammonia, he describes similar results with ammonium chloride at —75°, finding that hydrogen and chlorine escape at the poles, no nitrogen escaping. Hence the group NH_4 is unstable at —75°. He found the same results with ammonium iodide at —75°, while Hugot[6] finds that free iodine acts on liquid ammonia at —33°.5, forming the compound $NI_3.3NH_3$.

Moissan[7] studies the action of ammonium chloride on lithium-ammonium and calcium-ammonium dissolved in liquid ammonia at —75°. There were two possibilities:

I. $Ca(NH_3)_4 + 2NH_4Cl = CaCl_2 + 4NH_3 + 2NH_4$;

II. $Ca(NH_3)_4 + 2NH_4Cl = CaCl_2 + 6NH_3 + 2H$.

Both with calcium-ammonium and lithium-ammonium the reaction was as represented in equation II. The experimental details are very striking.

Moissan[8] tries the action of dry liquid hydrogen sulphide

[1] Moissan seems to consider NH_4 not as a metallic radical "ammonium" but rather as a metallic-ammonia hydride, or hydrogen-ammonium, in which case it belongs to one of these two series: NaH, KH, LiH, NH_3H, or KNH_2, $NaNH_2$, $LiNH_2$, HNH_2.

[2] Compt. rend., **132**, 510.

[3] *Ibid.*, **128**, 26.

[4] *Ibid.*, **133**, 713.

[5] Ber. d. chem. Ges., **34**, 2604.

[6] Ann. chim. phys., [7], **21**, 23.

[7] Compt. rend., **133**, 715.

[8] *Ibid.*, **133**, 771.

on the ammonium metals, as it might be possible that the reaction, $2(LiNH_3) + H_2S = Li_2S + 2NH_4$, might occur at low temperature. As a matter of fact ammonia and hydrogen are given off at —73°. In this experiment too, the beauty and ingenuity of the experimental work command admiration. Moissan concludes the article with these words: "Ammonium, which, in fact, only represents a theoretical conception intended to unify some formulas, does not seem to exist at —73° in the presence of liquid hydrogen sulphide."

Hydrides.

Until recently little was known of compounds of the alkali and alkaline earth metals with hydrogen. Hautefeuille and Troost, in 1874, studied the action of hydrogen on potassium and sodium, and found that these metals absorb hydrogen as does palladium, and that substances of metallic appearance are formed to which they assigned the composition K_2H and Na_2H. Winkler, in 1891, studied the action of magnesium on oxides of calcium, barium, and strontium, heated in a current of hydrogen, and believed, from the behavior of the resulting mixtures toward water, that hydrides of barium, strontium, and calcium were formed of the general composition, MeH. The univalence of these metals corresponding with the semivalence—if this term can be used—in the hydrides of sodium and potassium, Me_2H.

The first ray of light on this subject came from the fine work of Guntz on lithium and its derivatives. In an article[1] on lithium hydride he confirms Troost and Hautefeuille's observation that below red heat lithium absorbs seventeen times its volume of hydrogen without changing appearance; but he finds that if lithium is heated rapidly to a bright-red in an iron boat, in a current of hydrogen, it takes fire and burns, forming a fused, very hard, white mass, which analysis proved to be lithium hydride of the composition LiH. The fused hydride is not deliquescent; is scarcely attacked by cold air; heated in air it gives $LiO + H_2O$; it decomposes water, $LiH + H_2O = LiOH + H_2$. Heated in nitrogen it yields nitride and ammonia. The subject was not further investigated until 1890, when Moissan[2] made calcium hydride from pure calcium. It is much more active than lithium hydride. Its properties were very carefully studied. It has been already described in this JOURNAL.

Barium hydride was made in 1891, by Guntz,[3] by heating

[1] Compt. rend., **122**, 244.
[2] *Ibid.*, **127**, 29; Ann. chim. phys., [7], **18**, 289; This JOURNAL, **34**, 96.
[3] Compt. rend., **132**, 963.

barium amalgam in a current of hydrogen at 1200°. It is a grayish-white, fused, crystalline mass of the composition BaH_2. It was not quite pure, as he found it impossible to remove traces of mercury and of iron from the boat. When heated in nitrogen it decomposes at bright-red heat, forming nitride, as does the hydride of lithium, while calcium hydride is not attacked by nitrogen.

Strontium hydride was first made by Gautier[1] in 1901. The announcement was brief. Two weeks later Guntz[2] published his unfinished work on strontium and its hydride, which he obtained from strontium amalgam, but as yet quite impure. Two weeks after this Gautier published another article[3] in which he describes pure strontium hydride; he obtained it from a cadmium-strontium alloy, by heating very slowly in a magnesia boat, in a porcelain tube in a current of dry, pure hydrogen. The hydride was a white fused solid. Its reactions are similar to those of calcium hydride.

Potassium Hydride.—Moissan[4] recently made potassium hydride by heating potassium in a current of dry hydrogen in an iron boat in a glass tube, so that the under side of the tube is at 360°, while the upper side is cooler. The hydride sublimes and condenses as a tangled mass of snow-white crystals on the cooler side of the tube. When enough has collected the tube is cooled in a current of hydrogen, the boat slid back, and the part of the tube containing the hydride fused at both ends. Thus a tube of hydride is needed for every experiment, as it is so reactive that it can scarce be removed from the tube. It decomposes water, takes fire in cold oxygen, cold air, cold fluorine, and in cold chlorine. It is a violent reducing agent. It does not act on liquid ammonia, but if heated with gaseous ammonia yields amide, $KH + NH_3 = KNH_2 + H_2$. Analyses prove the absolute purity of the hydride.

He[5] makes potassium formate quantitatively by union of potassium hydride and carbon dioxide at ordinary temperature. He[6] makes ethane and methane quantitatively, by action of potassium hydride on ethyl iodide and on methyl chloride.

Sodium Hydride.—Moissan[7] made sodium hydride in the same way as the potassium hydride, which it resembles in appearance and reactions. The best temperature is 360°. He finds that if the boat be kept for some time at 360° the sodium

[1] Compt. rend., **133**, 1005.
[2] *Ibid.*, **133**, 1209.
[3] *Ibid.*, **134**, 100.
[4] *Ibid.*, **134**, 18.
[5] *Ibid.*, **134**, 261.
[6] *Ibid.*, **134**, 389.
[7] *Ibid.*, **134**, 71.

in the boat absorbs and dissolves some of the hydride, for if the sodium is dissolved in liquid ammonia a white substance remains undissolved which proves to be the hydride, though never quite pure, as in spite of all precautions it always contains traces of sodium oxide. Obtained by the sublimation method it is quite pure. E. RENOUF.

A New Method for the Preparation of Unsaturated Hydrocarbons.

In recent numbers of the *Berichte*[1] W. Ipatiew describes the results of a study of the pyrogenetic decomposition of alcohols. When the vapor of the alcohol was passed through tubes heated in a combustion furnace it was decomposed, the products depending upon the nature of the tube or the foreign substance placed in it. The decompositions can be expressed by the following equations:

$$(1)\ C_2H_5OH = C_2H_4 + H_2O;$$

$$(2)\ C_2H_5OH = CH_3COH + H_2.$$

If a glass or iron tube was used the amount of the unsaturated hydrocarbon formed was small. The introduction of stick zinc into the tube caused a considerable increase in the amount of aldehyde formed, amounting in some cases to a yield of 80 per cent. When, on the other hand, powdered zinc was used the yield of hydrocarbon was increased.

This suggested the possibility of securing some substance which would influence the reaction as much in favor of the formation of the hydrocarbon as stick zinc does in favor of the aldehyde.

Experiment showed that impure graphite, such as is used for crucibles, would give the desired results. If the vapor of the alcohol was passed through a glass tube containing the scraps of broken crucibles, which were heated to 600°, an energetic decomposition took place with the formation of the hydrocarbon and water. The results obtained in several experiments will give an idea of the yield. One hundred and fifty grams of ethyl alcohol were passed through the tube in thirty minutes and about half of the alcohol was decomposed. The ethylene was absorbed in bromine and 160 grams of pure ethylene bromide was obtained. Only about 1 gram of aldehyde was formed. In another experiment 127 grams of propyl alcohol was used, and in an equal time 160 grams of propylene bromide was obtained.

[1] Ber. d. chem. Ges., **34**, 3579 (1901); **35**, 1047 (1902).

Other alcohols acted in a similar manner showing the method to be a general one. The apparatus is quite simple, and if the temperature can be regulated there should be no difficulty in obtaining large amounts of the gases, as the graphite lasts for a long time and the process is a continuous one.

J. ELLIOTT GILPIN.

Barium Sulphate in Gravimetric Analysis.

"The exact determination of sulphuric acid as barium sulphate in no sense belongs among the simple and easy tasks as was early supposed, but requires great attention and great care."[1] In fact, the studies made before and since this became generally recognized (and which will be covered by this review) prove the extreme difficulty, if not impossibility, of precipitating barium sulphate pure.

The analytical value of barium sulphate was recognized very early, possibly first about 1750, by Bergmann,[2] and to this is likely due the fact that its composition received attention from Vauquelin,[3] Kirwan and Klaproth,[4] Aiken,[5] Berard,[6] Berzelius,[7] and others[8] prominent among the founders of quantitative analysis.

The ease with which it carries down with it salts and acids, of themselves soluble in water, and the difficulty of entirely removing these even by digestion with strong acids, are characteristic of it. "The precipitate produced in a solution containing sulphuric acid or sulphates by barium salts is never perfectly pure barium sulphate,"[9] and the "impurities are in a state of combination which cannot be broken up by an excess of acid."[10]

Records of difficulties due to the presence of various salts and acids exist in considerable number. Those due to magnesium salts and salts of weak bases, such as iron and copper, were discovered by Berzelius,[11] those due to alkaline sulphates by Turner,[12] to barium nitrate by E. Mitscherlich,[13] to

[1] Fresenius: Anleit. zur Quant. Chem. Anal., 6 Aufl., **1**, 391.
[2] Fourcroy's Chemistry, Heron's translation from 4th French edition, Vol. I., 321.
[3] Ann. chim. phys., [1], **50**, 168 (1804).
[4] J. für Chem. und Phys. (Gehlen), **5**, 515 (1805).
[5] Nicholson's Jour., **22**, 304.
[6] Ann. chim. phys., [1], **71**, 69 (1809).
[7] *Ibid.*, [1], **78**, 30 (1811).
[8] Fourcroy, Thenard, Richter, and Buchholz.
[9] H. Rose: Handb. Anal. Chem., 6th Ed., II., pp. 24, 25, 455 (1871).
[10] Berzelius: Ann. chim. phys., [2], **14**, 376 (1820).
[11] *Loc. cit.*; compare Fresenius: Ztschr. anal. Chem., **19**, 53 (1880); Jannasch: J. prakt. Chem., **147**, 333, foot-note (1889); Lunge: Ztschr. anal. Chem., **19**, 419; Gladding: J. Am. Chem. Soc., **17**, 398.
[12] Phil. Trans., **1**, 291 (1829); Compare Berzelius: Jahresbericht, 1831, p. 142; also discussion between Berzelius and Thomas Thomson; Jahresbericht, 1827, p. 77; Phil. Mag., (2), **4**, 453 (1828); *Ibid.*, (2), **5**, 221 (1829).
[13] Pogg. Ann., **55**, 209 (1842).

cerium salts by Marignac,[1] to barium chloride by E. Siegle,[2] to potassium chloride (and chlorate) by H. Rose,[3] to aluminium salts by A. Mitscherlich,[4] to platinum salts by Claus,[5] to lithium salts by K. Diehl,[6] to alkaline chlorates and nitrates by Fresenius,[7] to mixtures of alkaline chlorides and sulphates by Kretschy,[8] to ammonium and sodium sulphates and to vanadium compounds by H. Rose,[9] to potassium chloride by B. Schultze,[10] to zinc chloride by Jannasch and Richards,[11] to sulphuric acid by H. Rose,[12] to phosphoric acid by Scheerer and Rube[13] and by Spiller,[14] to organic acids by Jannasch and Richards.[15]

Substances are known that inhibit the precipitation. Chromium salts[16] may entirely prevent it, and ferric salts in hot solutions[17] behave in an analogous way, but quite feebly. Tartaric and racemic acids restrain it slightly, and alkaline citrates[18] very markedly. Nitric acid[19] (under certain peculiar conditions), and metaphosphoric[20] and metaboric[21] acids interfere similarly.

[1] Arch. des Sc. phys. et nat., **8**, 265; also Ann. Chem. (Liebig), **68**, 216 (1848).
[2] J. prakt. Chem., **69**, 142 (1856). Compare H. Rose: Pogg. Ann., **113**, 627 (1861); Mar: Am. J. Sci., [3], **41**, 288 (1891); Browning: *Ibid.*, [3], **45**, 403 (1893); Phinney: *Ibid.*, [3], **45**, 471 (1893). The last three articles illustrate admirably how one may be misled by errors from this source. Richards and Parker: Ztschr. anorg. Chem., **8**, 413 (1895). This article sets forth the results of a careful study of the difficulties and the best way of dealing with them.
[3] Pogg. Ann., **113**, 627 (1861).
[4] J. prakt. Chem., **83**, 455 (1861).
[5] *Ibid.*, **85**, 129 (1862); also Jahresbericht, 1861, p. 323.
[6] Ann. Chem. (Liebig), **121**, 98 (1862).
[7] Ztschr. anal. Chem., **9**, 52 (1870); compare Gladding: J. Am. Chem. Soc., **16**, 398 (1894).
[8] Ztschr. anal. Chem., **10**, 396 (1871).
[9] Handb. Anal. Chem., 6th Ed., II., pp. 368, 456 (1871).
[10] Wagner's Jahresbericht, 1882, p. 264.
[11] J. prakt. Chem., **147**, 321 (1889); compare Thiel: Ztschr. anorg. Chem., **22**, 424 (1900).
[12] Handb. Anal. Chem., 6th Ed., II., p. 455 (1871).
[13] J. prakt. Chem., **75**, 113 (1858).
[14] Chem. News, **10**, 219; also Jahresbericht, 1864, p. 695.
[15] J. prakt. Chem., **147**, 325 (1889); compare Spiller: J. Chem. Soc. (London), **10**, 110 (1858); Gladding: J. Am. Chem. Soc., **16**, 398; Küster and Thiel: Ztschr. anorg. Chem., **19**, 101 (1899).
[16] Recoura: Ann. chim. phys., [7] **4**, 494; Whitney: Ztschr. phys. Chem., **20**, 40.
[17] Fresenius: Ztschr. anal. Chem., **19**, 53 (1880); Lunge: *Ibid.*, **19**, 419 (1880); Gladding: J. Am. Chem. Soc., **16**, 398 (1894); compare Ostwald: Ztschr. phys. Chem., **20**, 340.
[18] Spiller: J. Chem. Soc. (London), **10**, 110 (1858).
[19] E. Schöne: Pogg. Ann., **112**, 214.
[20] Metaphosphoric acid calls for a more detailed consideration. Recently, Wiesler (Ztschr. anorg. Chem., **28**, 198 (1901)) called attention to the fact that he had no difficulty in analyzing barium metaphosphate, whereas Graham had stated that this acid partly prevents the precipitation of barium as sulphate. The reviewer has not yet found this statement in Graham's papers; in his well-known article read before the Royal Society two analyses of barium metaphosphate are described, but both yielded precipitates that were too heavy (Phil. Trans., 1833, pp. 253 to 284; also Pogg. Ann., **32**, 69 (1834); and Alembic Club Reprints, No. 10). The statements to be found in the text-books regarding this matter (Fresenius: Anleit. zur. Quant. Anal., 6th Ed., I., p. 152; H. Rose: Handb. Anal. Chem., 6th Ed., II., p. 555; Menschutkin: Anal. Chem. (trans. by Locke), 309) are based upon the experiments of Scheerer and Rube (J. prakt. Chem., **75**, 113 (1858)) which clearly showed the difficulty of complete precipitation in the presence of metaphosphoric acid; this was confirmed by Spiller's work (Chem. News., **10**, 219 (1864)). It might be suggested in explanation

In these cases there is more or less reason for the belief in the formation of double salts, or of "complexes" in the solutions, in which compounds the barium or the sulphuric acid, or both, are involved.

If it is possible to distinguish between such cases and those where other substances in solution (in some simpler way, perhaps) merely increase the solubility of the barium sulphate, we can distinguish a third class of substances whose presence, at least in any considerable amount, is to be avoided where barium sulphate is to be precipitated. Nitric[1] and hydrochloric acid,[2] alkaline[3] and ammonium nitrates[4] belong here. Under the conditions of most analyses, however, barium sulphate is very insoluble;[5] so, also, in water.[6]

In order to precipitate barium sulphate quantitatively, and in a form easily filtered and washed, and at the same time least impure, it is best to have the solutions which are to be mixed dilute[7] and hot,[8] to mix them very slowly and with constant stirring,[9] and to have the precipitant present in con-

that probably Wiesler had converted all of his meta acid into the ortho acid before the precipitation of barium sulphate was made, for Spiller found orthophosphoric acid to have no such influence. But Scheerer and Rube's statement that the precipitates formed in solutions containing metaphosphoric acid do not contain it, but the ortho acid, is confusing to this explanation. A second suggestion of an explanation arises from the fact that Wiesler was analyzing a trimetaphosphate, whereas the others referred to were analyzing hexmetaphosphates. Further, while Maddrell (Ann. Chem. (Liebig), **61**, 53 (1847)) mentions no difficulty in analyzing barium dimetaphosphate by heating with concentrated sulphuric acid, Ludert (Ztschr. anorg. Chem., **5**, 33 (1894)) obtained rather unsatisfactory results when he applied the same method to hexametaphosphates. If Fleitmann experienced difficulties in the analyses of barium metaborates, he avoided them by digesting the finely ground salt with a solution of sodium carbonate (Pogg. Ann., **78**, 361 (1849)).

[1] Horn: Dissertation, p. 52 (1900).

[1] and [2] Piria: Il Cimento, anno V., p. 257 (1847); H. Rose: Pogg. Ann., **95**, 109 (1855); Calvert: Chem. Gaz., 1856, p. 55; also Phil. Mag., [4], **11**, 390 (1856); Nicholson and Price: Phil. Mag., [4], **11**, 169 (1856); Noad: J. Chem. Soc. (London), **9**, 15 (1857); Siegle: J. prakt. Chem., **69**, 142 (1856); Gatkowsky: Ber. d. chem. Ges., **8**, 330; Erdmann and Mittenzwey: J. prakt. Chem., **75**, 214 (1858); Gladding: J. Am. Chem. Soc., **16**, 398 (1895).

[3] Fresenius: Ztschr. anal. Chem., **9**, 52 (1870).

[4] Erdmann and Mittenzwey: *Loc. cit.*

[5] Fresenius: *Loc. cit.* One part requires for its solution 400,000 parts of water. Fresenius (Ztschr. anal. Chem., **30**, 455 (1891)) carefully repeated his work and found one part required for its solution 401,000 parts of water (containing 1.1 per cent hydrochloric acid and 0.46 per cent sulphuric acid).

[6] Marqueritte (Compt. rend., **38**, 308 (1854)) had placed the solubility at 1 part in 200,000 parts of water, while Calvert (*Loc. cit.*) placed it at 1 part in 800,000 parts of water. Calculated from electrical conductivity experiments, its solubility in water is 1 part in 429,700 parts of water at 18° C., or 1 part in 320,000 parts of water at 37°.7 C., according to Holleman (Ztschr. phys. Chem., **12**, 131 (1893)). One part dissolves in 436,030 parts of water at 19° C., according to Kohlrausch and Rose (Ztschr. phys. Chem., **12**, 241 (1893)).

[7] Bunsen (Ztschr. anal. Chem., **10**, 396 (1871)) recommended that each 100 cc. yield 0.1 gram of barium sulphate. H. Rose: Handb. Anal. Chem., II., p. 454 (1871); the precipitate runs through the filter when precipitated from concentrated solutions. Richards and Parker: Ztschr. anorg. Chem., **8**, 421; the more dilute the solution the less barium chloride is enclosed by the precipitated sulphate.

[8] H. Rose: Handb. Anal. Chem., II., p. 455; the precipitate is purer when formed in hot solutions than in those at ordinary temperatures. Menschutkin: Anal. Chem. (trans. by Locke), p. 39; the precipitate is amorphous and runs through the filter when it has been formed in cold solutions.

[9] H. Rose: *Loc. cit.*, p. 454. Richards and Parker: *Loc. cit.*, p. 421; the precipitates enclose more barium chloride when the solutions are mixed quickly.

siderable excess[1] in the resulting mixture. The solution of the barium salt should always be added to that of the sulphate or sulphuric acid, and if it is permitted to flow down the wall of the beaker in which the sulphate solution is contained, and thus meet the latter in a broad, thin film, the precipitate is less impure than if the solution be added drop by drop.[2] It is customary to have present some[3] hydrochloric acid to aid in converting the precipitate entirely to the crystalline form.[4]

It is usual also to digest the mixture some time over a low flame,[5] and to filter only after the mixture has become cold.[6]

Various methods for removing the substances which barium sulphate has carried down with it have been suggested. Treatment with hydrochloric acid was tried and abandoned by Berzelius[7] as inefficient, and it has succeeded little better in the hands of other chemists.[8] Brügelmann,[9] however, recommends it as an aid in partially overcoming the errors due to enclosed substances. Solution of the impure precipitates in concentrated sulphuric acid, and reprecipitation by diluting these solutions was advised by A. Mitscherlich,[10] but it is self-evident that such a procedure is useless where barium salts constitute all or part of the impurity;[11] yet this method

[1] Berzelius: Lehrb. der Chemie, III., p. 105; when solutions containing equivalents of barium chloride and potassium sulphate are mixed, 2.25 per cent of the barium used remains unprecipitated. Compare Note 12, p. 495, of this report. Joulin: Ann. chim. phys., [4], **30**, 374; when solutions containing barium chloride and sodium sulphate at N/5000 dilution are mixed, 1/27 of the salts remain undecomposed after twenty-four hours; only after four days is the precipitation complete. H. Rose: *Loc. cit.*; an excess of barium salt hastens complete precipitation. Richards and Parker: *Loc. cit.*, p. 419; an excess of barium chloride diminishes the solubility of the precipitate and does not increase the amount of barium chloride enclosed.

[2] Richards and Parker: *Loc. cit.*, p. 420; otherwise the quantity of barium chloride carried down is greater. H. Rose: *Loc. cit.*, p. 455; if the sulphate separates in a liquid which contains no barium chloride in excess it is almost free from barium chloride. Compare with the following, where the reverse order is followed and recommended: Mar, Browning, and Phinney, Note 2, page 496 of this report. Their precipitates contained barium salts as impurities, because when "purified" by solution in concentrated sulphuric acid and reprecipitation they weighed more than before. Mar explained this as due to "residual contamination."

[3] Fresenius: Ztschr. anal. Chem., **9**, 52 (1870); if much hydrochloric acid is present it must be removed by evaporation, because it has great solvent action on barium sulphate. Richards and Parker: *Loc. cit.*, p. 420; the presence of much free hydrochloric acid "enormously" increases the amount of barium chloride enclosed.

[4] Ostwald: Scientific Foundations of Analytical Chemistry (trans. by McGowan), **22**, 197.

[5] Richards and Parker: *Loc. cit.*, p. 416; "about an hour."

[6] Compare Note 6, p. 497, of this report.

[7] *Loc. cit.*, Note 10, p. 495, of this report.

[8] H. Rose: *Loc. cit.*, p. 455; treatment with hydrochloric acid is "useless."

[9] Ztschr. anal. Chem., **16**, 22; after heating in a crucible the precipitate is treated with 3 or 4 drops of moderately strong hydrochloric acid, the lumps of the precipitate being broken up with a glass rod and the mixture warmed two minutes without boiling, over a gas-flame. The solution obtained is poured through a small filter and then the whole operation repeated several times until the filtered liquid remains clear when tested with sulphuric acid. Then the entire precipitate is brought upon the filter, washed with boiling water, dried, heated, and weighed.

[10] J. prakt. Chem., **83**, 458 (1861).

[11] This was pointed out at the time; see Jahresbericht, 1861, p. 845, foot-note; also later by Fresenius: Ztschr. anal. Chem., **9**, 52 (1870). Compare Richards and Parker: *Loc. cit.*, p. 413; also Mar, Phinney, and Browning: *Loc. cit.*

removes alkali salts so completely that the spectroscope fails to detect more than the merest traces of them.[1]

Digestion with an acetic acid solution of copper acetate, though recommended,[2] is also useless.[3] Barium sulphate can be freed from many substances by fusion with four or more times its mass of alkaline carbonates,[4] whereby the barium is completely converted to carbonate, which can be filtered off, washed, and dried, and weighed as such or converted into sulphate.

After a precipitate of barium sulphate has been washed and dried, a quite usual practice[5] is to remove the precipitate as completely as possible from the filter-paper upon which it was collected to a weighed crucible, and then to burn the paper on a platinum wire held over the crucible. Reduction may occur even then to a greater or less extent,[6] and if the paper be burned in the crucible the percentage of reduction may become very great.[7] Richards,[8] however, has found that if the crucible be kept at such a temperature that the paper completely chars without bursting into flame, no considerable reduction takes place then or in the subsequent burning out of the charred paper. If reduction occurs, the barium sulphide may be reconverted to sulphate by heating the precipitate in an open, tilted crucible, or by the addition of a drop of concentrated sulphuric acid,[9] and subsequent removal of the excess of the same by heating to constant weight.

Barium sulphate cannot be heated with safety above a dull-

[1] H. Rose : *Loc. cit.*, p. 27.
[2] Stolba : Ding. poly. J., **168**, 431 ; also Ztschr. anal. Chem., **2**, 390 (1863).
[3] Fresenius : Ztschr. anal. Chem., **9**, 52 (1870). H. Rose : Handb. Anal. Chem., II., p. 455.
[4] H. Rose : Pogg. Ann., **95**, 96. It is necessary to use from six to seven times the equivalent weight of potassium carbonate to insure complete conversion of the barium sulphate to carbonate. But six to seven times the equivalent weight of sodium carbonate does not give complete decomposition of the sulphate even after one and a half hours. However, on account of the lower molecular weight of the sodium carbonate, four times the mass of either carbonate is sufficient. The origin of the fusion method in analytical operations and its application to barium sulphate is not without interest, if only historical. Scheele, who discovered that heavy spar is barium sulphate, was unacquainted with the fusion method, and decomposed the mineral by heating with charcoal or honey (Scheele's Werke, II., p. 179). Marggraf is the first to record the use of an alkaline carbonate in analysis by fusion ; he used potassium carbonate to decompose "Bologne stone" (Marggraf's Chemische Schriften, Berlin, 1767, II., p. 135). Wiegleb was the first to recommend Marggraf's method for barium sulphate, but because he used only one and a half times the equivalent weight of potassium carbonate to one of barium sulphate, the decompositions were never complete (Crell: Neueste Entdeckungen in der Chemie, II., p. 14). Stromeyer later applied it to heavy spar (Stromeyer's Untersuchungen, p. 222). H. Rose (*Loc. cit.*) was the first to carefully work out the proper mass relations for complete decomposition.
[5] Fresenius : Ztschr. anal. Chem., **16**, 339.
[6] Hagar : "Untersuchungen," 2d Ed., I., p. 711.
[7] C. W. Marsh : J. Anal. Chem., **3**, 164 (1889). There may be from 2 to 22 per cent of the barium sulphate reduced, depending upon conditions.
[8] Ztschr. anorg. Chem., **8**, 417 (1895).
[9] Marsh (*loc. cit.*) suggested sulphuric acid as an improvement on Hagar's prior suggestion of nitric acid, because barium sulphide evolves sulphuretted hydrogen when treated with acids.

red heat. Over a blast-lamp it will lose in weight as much as 1 per cent in thirty-five minutes. It is then alkaline in reaction, the loss having been due to the escape of sulphur trioxide.[1]

D. W. HORN.

Gravimetric Determination of Sulphuric Acid in the Presence of Iron.

The precipitation of barium sulphate, quantitatively and in a pure form, is probably no where else of so great industrial importance as in the analysis of pyrites. The fact that iron salts interfere at times, if not always, in such analyses is a matter of great significance to those concerned therein, and one of interest to all chemists as a special, and probably the best known case of "occlusion" of impurities by a precipitate. Berzelius first observed this fact and was of the opinion (which it is believed this report confirms) that "it is necessary to begin by removing the oxide"[2] (of iron).

Four different ways of avoiding the difficulties incident to such analyses find expression in the methods which are recommended in the literature:

1. The separation of the iron and sulphur by fusion with some oxidizing flux.

2. The separation of the iron as hydroxide, by means of ammonium hydroxide, from the solution in which the sulphuric acid is to be determined.

3. The reduction of the iron in the solution to the ferrous condition, before precipitating the barium sulphate.

4. The retention of the iron in the solution by the addition of organic acids before the precipitation.

The first principle is involved in the Fresenius method,[3] by which the pyrites are fused[4] with a mixture of potassium nitrate and alkaline carbonates, and the sulphuric acid determined in the filtrate obtained by extracting the melt with cold water after removing from it all nitric acid. The method has been repeatedly tested[5] and seems to have become the criterion by which other methods are judged.

[1] **Boussingault**: Compt. rend., **64**, 1159 (1867); Ztschr. anal. Chem., **7**, 244; compare **Bunsen**: Ann. Chem. (Liebig), **111**, 262 (1859).

[2] Ann. chim. phys., [2], **14**, 376 (1820).

[3] Ztschr. anal. Chem., **16**, 339 (1877); also **Fresenius**: Anleit. zur Quant. Anal., 6th Ed., II., p. 453 (1896).

[4] Other reagents for decomposition have been recommended: Lime and soda, by **Hayes**: Amer. Chemist, **5**, 271; caustic potash and bromine water, by **Iles**: Ber. d. chem. Ges., **11**, 1187; soda and magnesia, by **Clark**: J. Soc. Chem. Ind., 1885, p. 329.

[5] **Fresenius**: *Loc. cit.*; Ztschr. anal. Chem., **19**, 53 (1880); **Lunge**: *Ibid.*, **19**, 419; **Jannasch and Richards**: J. prakt. Chem., **147**, 333 (1889). "For the exact analysis of pyrites, Fresenius' method of fusion, as our experiments indicate, is the best and only correct method." **Lunge and Obregia**: J. prakt. Chem., **148**, 241 (1889); Ztschr. angew. Chem., 1889, 476. **Gladding**: J. Am. Chem. Soc., **16**, 401 (1894); Chem. News, **70**, 182 (1894). **Lunge and Misslin**: Ztschr. anorg. Chem., **21**, 198 (1899).

It has been criticized as troublesome and tedious.[1] Further, the oxidizing flux attacks the crucible and the dissolved platinum may interfere with the subsequent iron determination,[2] and where coal gas is used in the burner over which the fusion is accomplished, the sulphur it contains may give rise to considerable errors.[3]

Lunge devised a method involving the second principle already mentioned. The original Lunge method[4] consisted in dissolving[5] the pyrites in aqua regia, evaporating this solution repeatedly with hydrochloric acid to get rid of nitric acid,[6] diluting the residue, and determining the sulphuric acid in this solution as usual. But the barium sulphate precipitates thus obtained are always rendered impure by the presence of iron compounds,[7] and weigh too much or too little, according to the heat to which they are subjected before weighing.[8] To avoid this, Lunge modified[9] his method, introducing the precipitation of the iron as hydroxide by ammonium hydroxide and determining the sulphuric acid in the filtrate therefrom. One can obtain excellent results by this modified "Lunge method," but many analysts have experienced difficulties in so doing, on account of the formation and retention of some basic iron sulphate in the ferric hydroxide precipitate. As a result of this, the method has often been condemned and as often vindicated.[10]

Because of this difficulty and to do away with the tedious washing of the ferric hydroxide, Gladding modified the "Lunge method" in that he directed, instead of washing out all sulphuric acid from the ferric hydroxide, to dissolve the precipitate in hydrochloric acid and then add barium chloride, collecting the sulphate obtained on the same paper as

[1] Lunge: "Sulphuric Acid and Alkali," I., p. 55; Ztschr. anal. Chem., **19**, 419; Gladding: J. Am. Chem. Soc., **16**, 399 (1894); Chem. News, **70**, 182.

[2] Jannasch: J. prakt. Chem., **147**, 334 (1889).

[3] Price: Ztschr. anal. Chem., **3**, 483 (1864).

[4] "Handb. der Soda Indus.," I., p. 96.

[5] Other solvents have been recommended: Fumic nitric acid, Fresenius: "Sulphuric Acid and Alkali," I., p. 52; nitric acid and bromine, Gladding: J. Am. Chem. Soc., **16**, 398 (1894); Chem. News, **70**, 181; see also Lunge: J. Am. Chem. Soc., **17**, 181 (1895); Chem. News, **71**, 132; and Gladding: J. Am. Chem. Soc., **17**, 397 (1895). Caustic soda solution and bromine, Drown: Chem. News, **43**, 89 (1881).

[6] Compare Fresenius: Ztschr. anal. Chem., **9**, 52 (1870).

[7] Fresenius: Ztschr. anal. Chem., **19**, 53 (1880); compare Lunge: *Ibid.*, **19**, 419.

[8] Jannasch and Richards: J. prakt. Chem., **147**, 321 (1889).

[9] Lunge: Ztschr. anal. Chem., **19**, 419 (1880).

[10] Jannasch and Richards: J. prakt. Chem., **147**, 333 (1889); *Ibid.*, **148**, 236 (1889). Lunge, Barbezat, and Obregia: *Ibid.*, **148**, 239; Ztschr. angew. Chem., 1889, p. 473. Gladding: J. Am. Chem. Soc., **16**, 398 (1894); Chem. News, **70**, 181. Lunge: J. Am. Chem. Soc., **17**, 181 (1895); Chem. News, **71**, 132. Gladding: J. Am. Chem. Soc., **17**, 397. Lunge: *Ibid.*, **17**, 772 (1895); Ztschr. anorg. Chem., **19**, 454 (1899). Lunge and Misslin: *Ibid.*, **21**, 198 (1899). Meineke: Ztschr. anal. Chem., **38**, 215; *Ibid.*, **38**, 351. Lunge and Bebie: Ztschr. anorg. Chem., **21**, 200; Pattinson: J. Soc. Chem. Ind., 1885, p. 329; *Ibid.*, 1890, p. 21.

that used in the first filtration. Lunge protested vigorously.[1]

The "Gladding modification" as such has probably never come into general use, but is now used in a form proposed by Küster and Thiel, which consists in omitting the collection of the ferric hydroxide on a filter, but dissolving it, as did Gladding, with hydrochloric acid after an excess of barium chloride has been added to the ammoniacal solution from which the iron was precipitated, but in which it is still suspended. This method has come through numerous tests and attacks.[2]

The idea of reducing the iron to the ferrous condition originated with Jannasch and Richards, in an analogy to titanic acid.[3] It seemed possible that ferrous salts would not be carried down by barium sulphate as were ferric salts. But after trying this plan, using zinc and hydrochloric acid[4] for the reduction, they abandoned it because the precipitates still contained not only iron, but also zinc compounds. A detailed study by Thiel[5] confirms this and indicates a further difficulty arising from the excess of zinc retaining some of the sulphuric acid. On the other hand, Heidenreich,[6] Meineke,[7] and Lunge and Bebie[8] have gotten excellent results by this method. The explanation of this apparent contradiction will only become apparent, probably, when not results alone but also experimental details are published by those who use this method successfully.

The fourth and last method was likewise applied first by Jannasch and Richards.[9] The organic acids[10] they used to "keep up" the iron were formic, acetic, and citric, but, nevertheless, the barium sulphate precipitates contained iron. Later, Gladding[11] tried and abandoned this plan, using citric acid. Küster and Thiel[12] used oxalic and tartaric acids with

[1] Gladding: J. Am. Chem. Soc., **16**, 401, 404; Chem. News, **70**, 182 (1894). Lunge: J. Am. Chem. Soc., **17**, 181; Chem. News, **71**, 132. Lunge and von Keler: J. Am. Chem. Soc., **17**, 183-186; also Ztschr. angew. Chem., 1895. pp. 71, 72. Gladding: J. Am. Chem. Soc., **17**, 399 (1895). Lunge: *Ibid.*, **17**, 775 (1895).

[2] Küster and Thiel: Ztschr. anorg. Chem., **19**, 98 (1899). Lunge: *Ibid.*, **19**, 455 (1899). Küster and Thiel: *Ibid.*, **21**, 73 (1899). Lunge and Misslin: *Ibid.*, **21**, 198 (1899). Meineke: Ztschr. anal. Chem., **38**, 209, 215; *Ibid.*, **38**, 351. Lunge and Bebie: Ztschr. anorg. Chem., **21**, 200 (1899).

[3] J. prakt. Chem., **147**, 322 (1889).

[4] Jannasch and Richards used other reducing agents also: metallic aluminium, metallic magnesium, and sodium amalgam. But the precipitates were always impure. Since then Johnson (Chem. News, **70**, 212 (1894)) proposed sodium hypophosphite as the reducing agent, but Lunge (J. Am. Chem. Soc., **17**, 187) has shown that Johnson's claims for this method are not borne out by experiment.

[5] Ztschr. anorg. Chem., **22**, 441 (1900).

[6] *Ibid.*, **20**, 233 (1899).

[7] Ztschr. anal. Chem., **38**, 209, 351 (1899).

[8] Ztschr. anorg. Chem., **21**, 200 (1899).

[9] J. prakt. Chem., **147**, 325 (1889).

[10] Some organic acids prevent complete precipitation. Spiller: J. Chem. Soc. (London), **10**, 110 (1858).

[11] J. Am. Chem. Soc., **16**, 339 (1894).

[12] Ztschr. anorg. Chem., **19**, 101 (1899).

fair success, but their precipitates were somewhat colored, hence impure.

The explanation of how some barium sulphate is retained by solutions of iron salts and how iron salts are carried down by barium sulphate has been the subject of considerable work and speculation. Jannasch and Richards furnished some evidence for the existence of a barium ferric sulphate[1] in the impure precipitates before they were heated. On heating, sulphuric acid was lost and ferric oxide left behind in the barium sulphate. Ostwald[2] suggested an analogy between heated solutions containing iron sulphate and those containing chromium sulphate. In the latter case there is evidence of the existence of complex ions or groups, in the hot solutions, which do not yield $SO_4^{=}$ in the presence of Ba^{++} ions. This analogy led Küster and Thiel to quite an elaborate study,[3] and to the assumption of the complex $(BaFe(SO_4)_2)$, as the form in which the iron enters the precipitates. Richards[4] took issue with them upon this point and upon the basis of Recoura's[5] and Whitney's[6] work on solutions of chromium salts as well as upon his own studies of "occlusion," favored the assumption of a basic complex, $Fe(SO_4)OH$. The results of Ostwald's suggestion are summed up in a statement to be found in Küster and Thiel's last article,[7] to the effect that it is impossible to decide what the complex is by the data at hand.

Schneider[8] has subjected the double salt idea[9] of Jannasch and Richards to an experimental test. The tenacity with which iron is retained by barium sulphate, even when treated with strong acids, suggested to Schneider that a barium ferric sulphate, if formed at all, must be very stable. So stable a salt should form with ease, and should form in larger and larger amounts, the more favorable the conditions for the contact of nascent barium sulphate with an excess of ferric sulphate. Schneider's experiments show, however, that when varying amounts of barium sulphate are precipitated in the presence of the same amount of iron and in the same volume of solution, after enough sulphuric acid is present to convert

[1] *Loc cit.*, p. 332.
[2] Ztschr. phys. Chem., **29**, 340.
[3] Ztschr. anorg. Chem., **22**, 424 (1900).
[4] *Ibid.*, **23**, 383 (1900).
[5] Ann. chim. phys., [7], **4**, 494.
[6] Ztschr. phys. Chem., **20**, 40; J. Am. Chem. Soc., **21**, 1075.
[7] Ztschr. anorg. Chem., **25**, 322 (1900).
[8] Ztschr. phys. Chem., **10**, 425 (1892).
[9] The idea of double salts to explain analogous difficulties with barium sulphate had been used by Turner (Phil. Trans., 1829, (4), p. 291) and Claus (J. prakt. Chem., **85**, 129 (1862)).

all the iron into neutral ferric sulphate, the percentage of iron in the precipitates becomes practically constant, with a value of about 1.24 per cent. Further the mass of ferric sulphate in the precipitates beyond this limit increases directly as the mass of barium sulphate. When a constant amount of barium sulphate is precipitated in the presence of varying amounts of iron in equal volumes of solution, experiment proves that an excess of ferric sulphate is without influence after the barium sulphate has once reached its maximum ability to retain iron. According to Schneider these experimental results clearly indicate that we have here to deal with a solid solution, the barium sulphate being able to dissolve ferric sulphate, but, like any other solvent, only able to dissolve it up to its own point of saturation—a perfectly constant proportion, no matter how great the excess of ferric sulphate present.

To one who has followed these matters carefully through the literature, either the "Fresenius method" or the "Lunge method" in the final form given it by Küster and Thiel, recommends itself as reliable for the determination of sulphur in the presence of iron. The "zinc reduction method" cannot be considered as trustworthy at present, and the "organic acid method" is unreliable. As to an explanation of the appearance of iron in barium sulphate precipitates, it seems unjustifiable to go beyond Schneider's conclusions until further experiments have been carried out. D. W. Horn.